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Cadmium, chromium and lead in environmental samples : speciation and determination

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ABSTRACT

CADMIUM, CHROMIUM AND LEAD IN ENVIRONMENTAL SAMPLES: SPECIATION AND DETERMINATION

by
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Heavy metals are important contaminants in many environmental media. This work focuses on the improvement of current methods for water and sediment analysis for three metals, cadmium, chromium and lead. Batch ion exchange was used for water speciation and a microwave assisted sequential extraction scheme was developed for sediment characterization. The developed methods were applied to a group of environmental samples.

The exchangeable species of these metals in water were preconcentrated on ion exchange resins. These include the bioavailable free ions and weakly complexed ions. Metals sorbed on particles and strongly complexed ions, less bioavailable, were eliminated. The method was more convenient as samples can be stored and are more easily transported. Slurry analysis was also found to be useful if needed.

The microwave sequential extraction method developed was much more rapid than currently used methods. It gave comparable results to the modified Tessier method for cadmium, and the lead and chromium results also gave useful information on the most bioavailable species.

Samples of water, sediment and biota from the Shark River showed some correlation between pollutant levels in water and sediment, although the study was not sufficiently extensive to yield many firm conclusions.

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by
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TABLE OF CONTENTS

TABLE OF CONTENTS
(continued)

Chapter **Page**

TABLE OF CONTENTS
(continued)

Chapter **Page**

TABLE OF CONTENTS
(continued)

Chapter **Page**

TABLE OF CONTENTS
(continued)

Chapter **Page**

TABLE OF CONTENTS
(continued)

Chapter **Page**

TABLE OF CONTENTS
(continued)

Chapter **Page**

LIST OF TABLES

LIST OF TABLES
(continued)

Table **Page**

LIST OF TABLES
(continued)

Table **Page**

LIST OF TABLES
(continued)

Table **Page**

LIST OF TABLES
(Continued)

Table **Page**

LIST OF FIGURES

LIST OF FIGURES
(continued)

Figure **Page**

LIST OF FIGURES
(continued)

Figure **Page**

CHAPTER 1

INTRODUCTION

Speciation is defined by IUPAC as a "process which yields evidence of the atomic or molecular form of an analyte". In environmental studies there has been an increased awareness of the importance of speciation of metals in terms of the toxicity, bioavailability, bioaccumulation, mobility, and persistence in the environment. Collection of total concentration data on metals is increasingly inadequate for determination of such qualities as, for example, sample toxicity.

Methods for speciation of metals in environmental samples can be considered to be functional, operational or chemical. Functional speciation separates metal species based on the way they behave in the environment. Availability to biota, or mobility in groundwater are examples of functional speciation. It is difficult to devise analytical methods which determine these properties for routine samples. Chemical speciation seeks to determine the actual chemical form in which the metals exist. For instance, separating metallic mercury from methyl mercury and ethyl mercury would yield chemical speciation. This, also, is generally difficult to carry out in complex environmental samples. Operational speciation is the method usually relied upon to differentiate among metal species in environmental samples.

Operational speciation methods attempt to separate the species by the particular experimental conditions under which they are extracted. Since the methods are experimentally defined, the conditions are very important and should always be fully

described. Small changes in conditions can lead to quite different conclusions. In spite of these limitations, the relative ease of carrying out these methods has led to their adoption for characterizing environmental samples. This work is aimed at the development and refinement of some of these methods.

1.1 Natural Water Samples

It has been shown by many investigators, that the most biologically available form of heavy metals in water are the dissolved free ions or metal species in a rapid equilibrium with free ions, that is, metals present in relatively unstable complexes. In unpolluted waters, trace metals such as lead, cadmium and chromium are usually present at sub-ppb levels. Therefore, preconcentration techniques are needed even with modern, highly sensitive GFAAS or ICP MS instruments.

In natural waters, trace metals are present in a wide range of chemical forms, in both the particulate and dissolved phases. The dissolved phase comprises the hydrated ions, inorganic and organic complexes, together with species associated with heterogeneous colloidal dispersions and organometallic compounds. In some instances these metals are present in more than one valence state. The particulate phase also contains elements in a range of chemical associations, ranging from weak adsorption to binding to the detrital mineral matrix. These species are able to coexist, though not necessarily in thermodynamic equilibrium with one another.

1.2 Sediment Samples

It is important to determine the biogeochemical and ecotoxicological species in which metals exist in a sample. The total concentration of a metal provides little information about the effects of environmental processes on the metals fate and behavior. It is difficult to determine the metals' bioavailability or the toxicity of a sediment sample based on its total concentration. A more sophisticated fractionation of the sediment samples based on the species distribution can help in understanding the behavior and fate of the metals.

Thermodynamic calculation techniques[1] and experimental techniques are used for the speciation of a specific element in samples. Experimental techniques such as selective extraction, in which the data are focused on the metals associated with a specific chemical component are widely studied. The associated metals are selectively transformed into a single species with selective extraction procedures. Three to eight different fractions have been widely studied in the past decade[2-9]. Five major types of extractants are used for the selective extraction procedures. These extractants are cation-exchanging extractants, carbonate-dissolving extractants, acidic, reducing extractants, extractants releasing organic-bound metals, and strong acid extractants.

Most of the sequential extraction procedures use the least aggressive reagent for the first treatment. NH_4OAc, pH 7 and $MgCl_2$ are most widely used for the exchangeable fraction of the sample on the first treatment. Removal of the carbonates present in the sample is the second treatment. Following procedures are for easily reducible substrates, for oxidizable materials to release organic bound metals, and for residual minerals respectively.

CHAPTER 2

LITERATURE SURVEY

2.1 The Speciation of Trace Elements in Waters

2.1.1 The Ecological Importance of Trace Metals Speciation

Speciation of an element is the identification and determination of individual physical-chemical forms of that element in the environment, which together make up its total concentration in a sample [10]. Knowledge of the forms that an element can have in natural waters is of primary importance because their toxicity, mobility, bioavailability and bioaccumulation depend on the chemical species [11-13]. So speciation studies are of interest to chemists doing research on the toxicity and chemical treatment of waters, to biologists inquiring about the influence of species on animals and plants, and to geochemists investigating transport of the elements in the environment.

Measurements of the total concentration of microelements in water provide little information on bioavailability or their interaction with sediments and soil particles. Most studies of the susceptibility of fish to heavy metal poisoning have shown that the free hydrated metals ions are the most toxic [10-12]. Ions, which are strongly complexed or associated with colloidal particles are usually considered to be non-toxic.

Unpolluted fresh or seawater usually contains low concentrations of toxic metal species, since most of the toxic ions are adsorbed on inorganic or organic particles. Anthropogenic pollution, however, may add metal to water in a toxic form , or may cause metals already present to be converted into more toxic forms. For, example, acidification of natural waters may release previously bound ions, increasing their toxicity. Changes in

the oxidation state of metal ions also may have a profound effect on their bioavailability and toxicity. Chromium(III), for example, is an essential dietary trace mineral, while Cr(VI) is considered toxic and carcinogenic. Likewise arsenic(III) is much more toxic than arsenic(V).

The most important reason for speciation measurements is to identify the metal species which are likely to have adverse effects on living organisms, including bacteria, algae, fish and mammals. The interaction of metals with intracellular components is highly dependent on chemical form. Some species may be able to chemically bind directly with proteins and enzymes, others may adsorb on cell walls, whereas others may diffuse through cell membranes and exert a toxic effect. Toxicity is organism dependent and occurs when an organism is unable to cope either by direct usage, storage or excretion, with additional metal concentration.

2.1.2 Types of Metal Species in Water

- *Simple hydrated ions (free metal ions).* It is well known that heavy metals in the free form are very toxic to living organisms. Free ions like Cd(II) and Cu(II) are the most toxic species to unicellular algae, probably because they form complexes with the ligands in the surface of the membrane as the first step of assimilation. It is possible that a change of their coordination chemistry takes place inside the cell.
- *Inorganic complexes* (e.g. $CaCl_2$, $PbCO_3$). It is known that, in general, in hard water alkaline carbonates usually reduce toxicity of heavy metals probably due to carbonate

complexation. Inorganic complexes of heavy metals with chloride are common in seawater and affect their bioavailability and bioaccumulation.

- *Metal organic compounds with low molecular weight.* (e.g. copper complexes with amino acids, alkylmetal compounds). The presence of organics in natural waters may sometimes completely change speciation. For example, organic exudes from bioorganisms can form strong complexes with heavy metals usually minimizing the toxicity of metals in natural ecosystems. However lipid-soluble organic complexes are usually toxic, sometimes more toxic than free ions. It has been shown that certain uncharged organic ligands facilitate the diffusion of metals through an artificial lipid bilayer. Alkyl complexes of lead and mercury are very toxic because they are lipid soluble and can pass through the biological membrane into the bloodstream.
- *Organic complexes with macromolecules* (e.g. with humic acids, polysaccharides, pigments, etc.) Complexation of heavy metals with large organic molecules generally reduces the toxicity of the metals to microbiota because these complexes cannot pass easily through the biological membrane. It was demonstrated that humic substances reduced both the acute and chronic toxicity of Cu to certain organisms. Humic substances clearly represent an important complexation and transport mechanism for heavy metal ions in natural water, although in acidic waters, metals may be released to the more biologically available free form.
- *Metal species adsorbed on colloids, particulate matter, and sediments.* Colloids and particles together with sediments generally have the highest level of heavy metals in

natural waters. Clay minerals possess surfaces that are predominantly negative and can adsorb cations at the pH of most natural ecosystems. The same happens to hydrous metal oxides that can exchange protons and hydroxyl ions for cations and anions respectively, thereby decreasing their uptake by microbiota. However, heavy metals adsorbed on solid surfaces can be redissolved due, for example, to acid precipitation or complexation with ligands from wastewater.

2.1.3 Environmental Factors Affecting Speciation

- *Redox conditions.* Under anoxic conditions, e.g., these found in some interstitial waters, deep waters and closed basins, speciation can change completely. For example, reducing conditions can lead to conversion of sulfate to sulfide, with the precipitation of sulfide salts such as PbS or CdS., which greatly reduces the bioavailability and toxicity of these metals. The redox potential of the environment also determines the oxidation state of some metals ions. Fe(III) can be reduced to Fe(II), Mn(VI) to Mn(II), Cr(VI) to Cr(III), and As(V) to As(III), which greatly influence the bioavailability and toxicity of these elements.
- *pH.* The values of pH can influence speciation either by shifting acid-base equilibrium and redox reactions or by competition between protons and ligand groups. Adsorption processes on solid particles are also pH dependent.
- *Inorganic salts.* Alkaline earth cations that exist in much natural water at high concentrations, can compete with heavy metals for the inorganic and organic groups.

Salts affect sorption, coagulation and precipitation processes, changing the forms of heavy metals in water.

- *Temperature and pressure.* These parameters affect stability of complexes and the rate of chemical reactions. Temperature and pressure affect photosynthesis and the type of bioorganisms present.
- *Synergistic and antagonistic effects.* The presence of several heavy metals that can compete for the same type of protein in a living organism might effect the toxicity and bioavailability of these metals.

2.1.4 Approaches for Speciation

The speciation of trace elements in natural waters is a difficult task because they exist in very low concentrations in a medium with several macrocomponents, often in nonequilibrium situations, and so different approaches can be used to increase the information about the system. The important point is that the operations involved in measurements might well alter the original conditions, thus, full details of the analytical procedures used are relevant to any estimate of the alteration done.

- *Determination in situ.* This method is the least disturbing to the composition of the system under study, but generally little information can be obtained because of the complexity of natural systems and the low concentration range of trace elements.
- *Determination in a natural pretreated sample.* This approach is used in order to have a simpler system, with more concentrated trace elements species and/or with fewer

concentrations of macrocompounds. This provides more detailed information, but conclusions might be distorted due to the absence of the macrocomponents and the change of concentration.

- *Chemical models.* In this approach a very simple system is used in the laboratory as a first approximation to the real sample, followed by the addition of other compounds in order to study their influence on the previous model. These studies should be made under well-controlled conditions of temperature, pressure and ionic strength, since these parameters influence the values of constants and consequently the speciation results. In spite of the considerable interest of these studies in the understanding of the chemical reactions in natural media, their application as "models" of complex natural systems cannot be made without significant adaptations.
- *Computer modeling* involves the quantitative determination of each species by means of computer programs, generally assuming equilibrium conditions. For this calculation it is necessary to know total concentrations of metals, organic and inorganic ligands, colloids and particulate matter as well as stability constants of the complexes formed in solution and adsorption constants. Computer models generally assume equilibrium in waters. However, in nature, some reactions do not attain equilibrium during the residence time of the water. The residence time of most trace elements is usually controlled by sedimentation due to adsorption, coprecipitation, and uptake by organisms, and ion exchange.

In order to distinguish diverse group of species with different kinetics of dissociation, it is important to know the time scale of the analytical technique used and to compare it with the dissociation rate of the complex. In this context two different categories of complexes, inert and labile can be defined. The kinetics of dissociation of inert complexes is too slow compared with the time of analytical measurement. This situation has been observed in complexes adsorbed on particles, and with metals ions strongly bound to large molecules. The kinetics of dissociation of labile complexes is fast enough so that a thermodynamic equilibrium between a complex and the free ion is always reached during the measurement time. The distinction between inert and labile is not absolute for each compound and depends on the time scale of the analytical technique. Complexes with an intermediate behavior are called quasi-labile.

2.1.5 Methods of Speciation

Many analytical methods determine only the total concentration of the element in the sample, and a pretreatment procedure is generally required for speciation. Table 2.1 presents the most important methods of speciation.

For any speciation method, sampling methods and storage conditions for the water samples are extremely important. Sampling and storage procedures for determination of trace elements are reviewed elsewhere [11,12]. Teflon or polyethylene sampling containers are recommended. These should be decontaminated by soaking in 10% HNO_3 for 48 hours, then rinsed with distilled water and also with the sample. Acidification and

freezing can induce irreversible changes in trace elemental species, and samples should be stored at 4°C. A clean room or at least a special room with a filtered air supply is necessary for work at ultratrace levels.

2.1.5.1 Physical Methods of Speciation: In physical techniques the separation is based mostly on size fraction. After the application of the separation methods, the elemental content of each fraction can be determined. Analytical techniques for the determination of the total element concentration (such as Atomic Absorption Spectrometry, Graphite Furnace Atomic Absorption Spectrometry, Inductive Coupled Plasma Electronic spectrometry, Inductive Coupled Plasma Mass Spectrometry) can be used.

Table 2.1 Methods of Speciation

Physical Techniques – based on size, density or charge of the species	Centrifugation Ultrafitration Dialysis Gel Filtration Chromatography
Chemical Techniques – based on redox, complexation , and/or adsorption properties	Oxidative destruction of organics Liquid Extraction Ion-Exchange and Adsorbent Resins Voltammetry
Species Specific Techniques -applied to particular species	Potentiometry with specific electrodes GC and/or hydride generation HPLC
Bioassays – influence of the metal ion on the growth or inhibition of organisms	
Comprehensive Speciation Schemes-combinations of different methods of speciation.	

Physical methods of speciation (centrifugation, filtration, ultrafiltration, and dialysis) are extensively reviewed in the literature [10-12,14]. In environmental

procedures, filtration through 0.45 μm membrane is usually used in order to distinguish "particulate" and "soluble" trace element fractions and this method is discussed in some detail below.

The routine EPA procedures for toxic heavy metals such as cadmium, lead, copper, zinc, and nickel in natural waters requires filtering of the water sample through a 0.45 μm filter, acidification of the filtrate with nitric acid to release complexed and colloidally bound metals, before transportation to the laboratory for analysis. By convention, dissolved metal is considered to include any metal species which passes through a 0.45 μm filter. Some of the possible forms for a divalent trace metal in water are listed in Table 2.2 [11].

Table 2.2 Physical-Chemical Forms and Sizes of Various Species in Natural Waters

Physical-chemical Form	**Examples**	**Approximate diameter, nm**
Particulate (retained by the filter)	--	>450
Simple hydrated ions	$Cd(H_2O)_6^{-2}$	0.8
Simple inorganic complexes	$Pb(H_2O)_4Cl_2$	1
Simple organic complexes	Cu-glycinate	1 – 2
Stable inorganic complexes	PbS, $ZnCO_3$	1 – 2
Stable organic complexes	Cu-fulvate	2-4
Adsorbed on inorganic colloids	Cu(II)-Fe_2O_3, Pb(II)-MnO_2	10 – 500
Adsorbed on organic colloids	Cu(II)–humic acid	10 – 500
Adsorbed on inorganic/organic mixed colloids	Cu-(II)–humic acid/ Fe_2O_3	10 – 500

Many colloidal particles will, therefore, be found in the so-called dissolved metal category, as they will pass through the 0.45 μm filter. Perhaps filterable would be a better designation for these species, but this would require further definition, as the filter pore

size would also have to be specified. There is increasing evidence [14,15] that iron oxide and clay particles combine with humic acid to form colloidal particles which strongly adsorb heavy metal ions, thus controlling their presence in the free state in natural waters.

Filtration processes present some problems due to contamination of the filters and losses of trace compounds by adsorption, which is significant in environmental samples with low trace element concentration. Colloids whose diameter is smaller than of the filter can be retained due to adsorption and/or coagulation. These phenomena depend on the chemical nature of surfaces involved and hydrodynamics of the filtration process.

Recent field and laboratory experiments [16] demonstrated that a number of factors associated with filtration other than just pore size (diameter, manufacturer, volume of sample processed, amount of suspended sediment in the sample) can produce significant variations of the "dissolved" concentrations of Fe, Al, Cu, Zn, Pb, Ni and Co in natural waters. As such, simple filtration of unspecified volumes of natural water through unspecified 0.45 μm membrane filters may no longer represent an acceptable definition for a number of dissolved chemical constituents. It is also obvious that the term "dissolved" to describe the chemical concentrations associated with filtered water is misleading.

2.1.5.2 Chemical Methods of Speciation: Lipid soluble compounds, known to be highly after extraction toxic, can be at least roughly estimated by liquid extraction with organic solvents such as chloroform and hexane-butanol, which have dielectric constants similar

to these of biological membranes. The metal content in these fractions is determined. Some authors discuss separately hybrid methods of speciation [17,18]. In a hybrid technique the separation process and elemental detection occur on-line. The two techniques must therefore be coupled by an interface and the separation process has to be compatible with detection system. The separation process in this system is usually some form of chromatography, but the detectors normally used for chromatography lack the selectivity and sensitivity required for speciation studies. The favored detectors for hybrid systems are the sensitive element specific detectors (flame AAS, GFAAS, ICPES, ICPMS, etc.). On-line separation processes for trace elements or their complexes mostly include Gas Chromatography, High Performance Liquid Chromatography. Characterization of these hybrid methods is beyond the scope of this review and can be found in the literature [10,13,18,19].

2.1.5.3 Comprehensive Speciation Schemes: Various combinations of the physical and chemical methods discussed above have been proposed as speciation schemes for trace elements in natural waters.

Figura and McDuffie, using Anodic Stripping Voltammetry (ASV) and Chelex-100 resin in the column and in batch techniques, developed a speciation method based on the kinetics of the species [20,21]. The filtered sample was divided into two parts: one part was analyzed by ASV at pH=4 and the other was passed through a Ca-Chelex column with a flux of 2.7 ml/min. The heavy metals retained in the column were eluted

with HNO_3, partially neutralized with NH_4OH, then analyzed by ASV. The species not retained by the column were stirred with a Ca-Chelex for 3 days, then filtered and analyzed by ASV after digestion with HNO_3+$HClO_4$. The species retained by the batch technique were eluted by HNO_3 and analyzed by ASV method. Using this methodology, authors were able to establish a speciation scheme for Pb, Cu, Cd and Zn in samples of rivers, estuaries and wastes. The time scale of the techniques in the experimental conditions used was 2 msec for ASV, 7 sec for the column Chelex method and 3 days for the batch method. The authors found that Cd and Zn generally predominate in more labile forms than Pb and Cu. It has been noted that the scheme does not provide mutually exclusive separations. The "very labile" fraction measured by ASV is not necessary fully retained by the Chelex column, giving erroneous "moderately labile" numbers by difference. Nevertheless, it is likely that this type of approach could be useful in relating to bioavailability.

The scheme proposed by Batley and Florence [11] combines ASV measurements before and after passage of the sample through a Chelex-100 column, after UV radiation and after passage of UV radiated sample through Chelex -100. It enables up to seven classes of metal samples to be quantified. The scheme is based on the findings that Chelex-100 will differentiate free or weakly complexed metal ions from metals connected with colloidal particles. Colloids are unable to penetrate the pore network of the resin, and metals in strong complexes are unable to be dissociated during the time scale for the sorption separation. A criticism of this type of speciation scheme is that the results it

generates are operationally defined and are therefore difficult to interpret in terms of bioavailability.

The scheme proposed by Hart and Davies [22] does not attempt to separate exclusive classes, but defines filterable, dialysable and exchangeable metals. Dialyzable metals are concentrated on Chelex-100 resin during a continuous 5-h dialysis, while exchangeable metals are obtained by 24 hours equilibration with Chelex-100. Questions remain about how these data should be evaluated in the terms of bioavailability.

Other speciation schemes are described in the recent monographs [10-12]. Comprehensive speciation procedures are valuable tools for investigation of trace metal species in natural waters. However, as a rule these procedures are time and labor consuming which preclude their application to routine analysis. Some of them are limited only to specific waters or elements; others are not easy to evaluate in the terms of metals toxicity and bioavailability.

2.2 Aqueous Chemistry of Lead, Cadmium and Chromium

Dissolved trace elements in natural waters, such as Pb, Cd, Zn , Cu, have been extracted from natural waters with ammonium pyrrolidinedithio carbamate or dithizone dissolved in methylisobuthylketone [11,17]. All naturally occurring soluble complexes with most heavy metals in natural waters are likely to be dissociated and extracted by these compounds. The nonextractable fraction consists most probably of trace elements adsorbed or occluded on inorganic and organic particles and colloids.

Of the available methods for concentrating specific metals from water, ion exchange is attractive. Adsorption of the species of interest on ion-exchange or other adsorbent resin can concentrate them so that the analysis can be carried out with little manipulation of the sample, and thus with less chance of contamination. Conventional cation and anion exchange resins have been used for speciation of heavy metals, but iminoacetate chelating resin, such as Chelex-100 (Bio-Rad Co.) has been found to be even more suitable for this use. Columns packed with uncharged adsorbents (e.g. hydrophobic copolymers) have been also used for specific hydrophobic complexes of trace metals present in waters. Retained species are eluted with organic solvents, though it has been noted that in some systems (e.g. seawater) the recovery of metal-containing organics is not always quantitative. Since speciation and preconcentration of trace elements on ion-exchange and chelate resins is the important part of this study, the literature devoted to this topic is reviewed in more detail in section 2.3.

The first part of this investigation is focused on the speciation, preconcentration and analytical determination in fresh surface water of three metals of environmental concern, namely lead, cadmium and chromium. For better understanding of analytical procedures for their determination the aqueous chemistry of Pb, Cd and Cr is briefly discussed below.

2.2.1 Cadmium

Aquatic ecosystems are particularly sensitive to cadmium pollution because of the very low levels of this toxicant in prehistoric times and the strong tendency of the food web to

bioaccumulate this element. The properties of cadmium in the aquatic environment are discussed in detail in the literature [23,24].

The chemistry of cadmium in fresh water is complex depending on its speciation, which in turn is determined by the oxidation status, pH and the concentrations of numerous organic and inorganic anions and other cations. The stable state of cadmium in the natural environment is Cd(II) cations. In fresh waters cadmium is present totally as the divalent species up to pH 8, in the absence of precipitating anions such as sulfide and phosphate. Cadmium begins to hydrolyze at pH 8-9, forming $Cd(OH)^+$ species. Higher hydroxyl species are not relevant at the pH values commonly found in the environment. Cadmium forms chloride complexes in water. At low chloride concentrations cations $CdCl^-$ prevail while in seawater $CdCl_2$ and $CdCl_3^-$ are formed.

The mobility of cadmium in soil pore water and groundwater is strongly controlled by precipitation (as $CdSO_3$ and CdS) and by adsorption by soil particles. Adsorbability is generally greatest for iron hydroxides and least for clay minerals. The presence of soluble complexes of cadmium can considerably reduce adsorption.

Cadmium is an oxyphilic and sulfophilic element. It forms weak to moderately stable complexes with a variety of organic compounds. The organic matter found in natural water, including amino acids, polysaccharides, and carboxylic acids of aliphatic and aromatic nature contains suitable sides for complex formation with cadmium. Binding of cadmium to humic substances in waters was studied [25]. In typical lake water, humic acid complexation of cadmium accounted for only 2.7% of total cadmium. It was found that fresh groundwater generally contains a greater proportion, up to 90%, of

free Cd(II) cations than sewage effluents (62-71%) [26]. The dominance of Cd(II) species in a contaminated lake was reported[27]. Concentrations of dissolved and particulate cadmium in rivers and lakes found in the early eighties are reviewed in the literature [23] (Table 2.3). Dissolved cadmium levels in freshwaters generally range from 10 to 500 ng/L. It is evident that preconcentration methods in combination with modern instrumentation are needed for reliable determination of cadmium at these levels.

Cadmium is generally regarded as being dominated by dissolved forms except for situations where the concentration of suspended particles is high. It has been mentioned that the concept of "dissolved metals" is ambiguous and that species which pass through a 0.45 μm membrane may include ions, complexes and colloids.

Table 2.3 Average Concentrations of Dissolved and Particulate Cadmium in Rivers.

River	Dissolved Cd, ng/L	Particulate Cd, mg/kg
Elbe	150	2
Rhine	400	16
Mississippi	15	0.6
St. Lawrence	110	1.7
Hudson	250	6

Adsorption to sediments and particulate matter increases with pH. Addition of ligands which yield cationic complexes suppresses precipitation of Cd hydroxide, yet the sorption increases with increasing pH. Formation of an anionic complex (e.g. with EDTA) results in zero uptake of cadmium over a wide pH range. Cadmium residues in freshwater sediments are highly variable, ranging from 0.1mg/kg dry weight to 3000 mg/kg and more in the vicinity of Cd-Ni battery factories.

In fresh water, the total cadmium concentration consists of cadmium in ionic, colloidal, complexed, and particulate forms. However, the bioavailability of cadmium is not related to the total concentration. By convention, the particulate fraction is separated from the dissolved one by filtration through 0.45 μm membrane. Dissolved cadmium is known to exist in fresh waters mostly in the bioavailable free ionic form [25,27], although its speciation can be influenced by factors such as water hardness, pH, redox potential organic, matter and suspended particles [28,29].

2.2.2 Lead

The behavior of lead in natural waters is a combination of precipitation, equilibrium, and complexing with inorganic and organic ligands. The degree of mobility of lead depends on physical-chemical state of the complexes formed. Lead forms moderately strong chelates with organic ligands containing S, N, and O donor atoms. Lead also binds to different microbial growth media.

Many environmentally important lead compounds such as halides, sulfates, sulfides, phosphates and hydroxides are insoluble and thus are of relatively low toxicity in aquatic systems.

Concentrations of soluble lead in uncontaminated fresh waters are generally less than 3 ppb. The concentration of lead in prehistoric Antarctic ice deposits is 0.5 ng/L, which shows that anthropogenic pollution has significantly affected all aquatic ecosystems.

Physical-chemical speciation of lead in surface and drinking water indicates little or no free ionic lead. However, lead used to be a constituent of solder and some pipe-joint formulations, so that household water may have some contact with lead. Water which stands in household plumbing may accumulate spectacular levels of lead.

A significant portion of lead is bound to colloids, other hydrous iron oxides or organic macromolecules depending on the composition of the water. A substantial fraction of lead in the filterable (0.45 μm) fraction is not ion-exchangeable. The calculated equilibrium distribution showed that the most significant form of inorganic lead in river water is $PbCO_3$ (generally 80-90%) with smaller contribution from Pb^{2+} and $Pb(OH)^+$. Although Pb^{2+} and $Pb(OH)^+$ ions are present in equal concentrations at pH=6, $Pb(OH)^+$ predominates at pH=8. This latter ion has a different affinity for sorption sites than Pb^{2+}. Insoluble $Pb(OH)_2$ is not formed until the pH reaches 9.5-10.0. The contribution of ionic lead significantly increases at low pH, especially at pH<5. The two main forms of inorganic lead in seawater are $PbCO_3$ (83%) and $PbCl_2$(11%) [11]. From a review of lead speciation in different fresh waters, it was found that 40-80% of total lead was present in particulate forms [24]. Pb-organic complexes become significant at ligand concentrations above 10^{-5}M.

Despite more severe restrictions coming to force in many countries, the use of tetraalkyllead (TAL) as an antiknock agent still represents about 5-7% of the total world lead production [30]. The harmful effects of organolead compounds are considered to be

much larger than those of inorganic lead. The toxicity of alkyllead diminishes in the sequence $R_4Pb > R_3Pb+ > R_2Pb^{2+} > Pb^{2+}$; where $R = C_2H_5$ or CH_3.

The ionic form is much more persistent in the aquatic environment. Similarly, methylated lead species are less toxic than corresponding ethylated compounds, but more stable, volatile, and of longer half-lives. The chemistry of TAL compounds and their analytical determination are reviewed in the literature [30,31]. Data demonstrate that despite the consumption of TALs as gasoline additives, the major part of the total lead pollution results from inorganic forms.

2.2.3 Chromium

The concentration of chromium in unpolluted natural waters is usually low (less than 1 ppb). Chromium may be present in water in the trivalent or hexavalent form. In less oxidizing environments, Cr(III) is the prevalent species. It can exist as Cr^{3+}, $Cr(OH)_2^+$, $Cr(OH)_3$ and $Cr(OH)_4^-$ depending on the pH. At pH above 4, the solubility of Cr(III) decreases drastically and these ions readily precipitate at neutral to alkaline pH values. Cr(III) tends to be virtually immobile in most groundwater because of its low solubility, and because it is generally adsorbed by clay minerals, which typically have high cation exchange capacities at low pH values. Cr(III) readily forms complexes with a number of different ligands and their mobility would probably be enhanced due to decreased adsorption or increased solubilities of complexed species.

The Cr(VI) species, to be exact the $HCrO_4^-$ and CrO_4^{2-} anions, are generally considered to pose the greater risk to human health because they are more toxic, more soluble and more mobile in soil and solid wastes than Cr(III) species [32,33]. Therefore, measurements of the concentration of Cr(VI), rather than total chromium, are a more appropriate indicator of water pollution. There are no significant solubility constraints on the concentration of Cr(VI) in water. Two mechanisms are thought to control the mobility of hexavalent chromium: 1) Cr(VI) reduction to Cr(III), which is rapidly precipitated, and 2) adsorption of Cr(VI) to positively charged soil surfaces, with adsorption decreasing with increasing pH.

The problem with the determination of Cr(VI) in environmental samples is its delicate equilibrium with Cr(III). These species can be converted from one form to another as a result of redox reactions depending on pH, oxidation potential, various impurities and microorganisms. In the natural aquatic environment, the main significant redox couples are: H_2O/H_2(aq.), Mn(II)/Mn(VI), Fe(II)/Fe(III), NO_2^-/NO_3^- and S_2^-/SO_4^{2-}. It is practically impossible to predict the potential likelihood and the rate of redox reactions between trivalent and hexavalent chromium in natural water because of a myriad of parameters affecting the process.

Cr(III)/Cr(VI) redox reactions may occur during sample preparation, transportation, and storage. Therefore, it is highly preferable to perform the determination of Cr(VI) in water samples, or at least the speciation step, in the field.

It is inevitable that in the near future, water-quality legislation for toxic heavy metals like cadmium, lead and chromium, will include requirements for speciation. It may be possible to tolerate higher total concentrations of some metals as long as the labile fraction is below a certain limit.

2.3 Speciation of Trace Elements on Ion-Exchange Resins and Their GFAAS Determination

2.3.1 Sorption of Trace Elements on Ion-Exchange and Chelating Resins

The determination of trace metals in natural water samples often involves preconcentration and/or separation procedures. The sensitivity of even GFAAS and ICP MS is insufficient for accurate determination of the most ultra-trace elements. Furthermore, salts and undissolved particulate cause interference with the determination of trace elements. Therefore it is necessary to concentrate the analyte before determination, and, if possible, to separate the analytes from dissolved major matrix constituents and particulates. Solvent extraction, coprecipitation and sorption on ion-exchange resin are the most widely used methods [11,12,17]. The ion-exchange technique, especially with application of chelating resins for trace element preconcentration, is discussed below.

The main advantage of ion exchange for preconcentration of water samples is that large concentration factors (100 times and more) can be obtained and the bulk of the matrix removed. Drawbacks include variable blanks and the fact that sometimes the technique can be time-consuming. In most cases, the preconcentration of lead and

cadmium from natural water is done under dynamic conditions by passing the sample through a sorbant - packed column. The analyte is then eluted from the sorbent with a small amount of a high purity acid [17,34,35]. In recent years, the use of chelating exchange resins (e.g. Chelex-100) for preconcentration of trace metals in waters, especially in seawater, has become popular [11,17,34,35]. Chelex-100 is a copolymer of vinylbenzyliminodiacetic acid, styrene and divinylbenzene, and shows strong chelating activity for various trace metals, particularly for Cd(II) and Pb(II) ions. There are many published examples of use of this resin for preconcentration and separation of ionic Pb, Cd, Cu, Zn, Ni and Cr(III) from natural waters. Chelex binds ionic metals strongly, but since its pore size is only 1.5 nm, large complexes and colloids are not retained on the resin beads. It was shown that solutions of colloidal hydrated ferric oxide and bulky organic dye molecules are quantitatively rejected by the resin [36]. This resin, therefore provides a simple and efficient method for preconcentration and separation of heavy metals in cationic form from colloidally associated species and metals present in strong complexes.

The concentration technique for trace metals in seawater with the Chelex-100 resin can be summarized as follows [35]. The resin (100-200 μm mesh, Na form) was cleaned with acid, rinsed and changed to the ammonia form. The Chelex resin was packed in a small disposable polyethylene column. Analytes in seawater samples were preconcentrated with the resin immediately after sample collection onboard ship. Seawater was pumped through Teflon tubing into the column at a flow rate of 2-3 ml/min. After pumping had been completed, the column was capped at both ends,

wrapped in polyethylene, and frozen for storage. After return to the lab, the resin was thawed and eluted with 30 ml of 2M HNO_3. The concentration factor was about 120. The treated effluents were analyzed by GFAAS. The recovery of trace metals for this Chelex procedure was performed with ^{65}Zn and ^{115}Cd spiked seawater samples and found to be almost 100% providing rather accurate and reliable results for trace metals. The drawbacks of this technique are a long preconcentration time, and some complexity of the system for installation in remote sites.

Haraldsson et al [37] investigated multi-element speciation of trace metals in fresh water using microcolumns packed with three sorbents: Chelex-100, Fractogel DEAE 650 and Sep-Pak C-18. Trace metal concentrations were compared in water before and after sorption on columns by ICP MS method. 15 ml of a sample were collected after passing through 1 ml of a sorbent at a flow of 2 ml/min. Therefore, the time of contact of samples with sorbents was relatively low. It was expected that Chelex would adsorb free metal ions and ions in labile complexes that dissociate during the time of contact with the resin. Sep-Pak traps non polar organometallic compounds, while Fractogel retains humic complexes and metals bound to them. It was concluded that the method does not provide a clear-cut distinction between different forms of metal species, but gives some valid information for understanding the natural behavior of trace metals in water. The attempt to prepare a speciation standard was not successful.

Preconcentration using a Chelex-100 microcolumn and ICP MS analysis enables the determination of lead isotope ratios and lead concentrations in seawater [38]. Chelex-

100 was also used for preconcentration and radiochemical separation by neutron activation analysis [39].

Recently US EPA (Office of Water) has released manuals for determination of some *total trace elements* in ambient waters by on-line chelation preconcentration and GFAAS or ICP MS measurements [40,41]. Speciation procedures are not discussed there. Method 1637 is applicable to Pb and Cd and Method 1640 to Pb, Cd, Cu, and Ni. The methods are intended to be performance based, and the laboratory is permitted to omit any step or modify any procedure as long as all performance requirements in these methods are met. An iminodiacetate functionalized chelating resin is used to preconcentrate trace elements. The recommended sorption method was developed earlier [42,43]. Following acid solubilization, the water sample is buffered (pH 5.5) before it enters the chelating column. Group I and II metals and the most anions, are separated from the analytes by elution with ammonium acetate at pH 5.5. The analytes are subsequently eluted into a simplified matrix consisting of 0.75M nitric acid and are determined by stabilized temperature GFAAS or ICP MS. Procedures for sample preparations and analysis including quality control are described in the manuals in detail. EPA found that one of the greatest difficulties in measuring pollutants in these levels was precluding sample contamination during collection, transport and analysis.

Along with preconcentration on columns packed with ion exchange and chelating resins, sorption of heavy metals in batch conditions is used. In our opinion, the batch procedure is more convenient for field studies. Sorption on fine ion-exchange beads in static conditions can be easily performed on site and is usually faster than sorption in a

column packed with the same resin. After filtration, beads loaded with heavy metals can be transported for analysis or analyzed in a mobile lab. Metal ions are evenly distributed on fine ion-exchange beads and samples can be analyzed directly in slurry without an elution step.

Chu at al. [44] preconcentrated Al, Cd, Cu, Fe, Mn, Ni, Pb, Ti and Zn from seawater using Chelex-100 resin followed by ICP-AES measurement. They evaluated and compared two techniques, i.e. column and batch preconcentrations. In the column method, a one liter sample of seawater was filtered and the pH of solution was adjusted to pH 5.5-6 with ammonium acetate solution. The seawater sample was passed at a flow rate of 2 ml/min through the column. For removal of matrix salts, the column was treated with ammonium acetate buffer (pH 6) and ultra-pure water. Trace metals collected on the resin were then eluted with 25 ml of 2M HNO_3 solution into a Teflon beaker. The eluent in the beaker was heated to dryness on a hot plate, and then the residue was dissolved with 5 ml of 0.2M HNO_3. The procedure for the batch preconcentration (100 fold) was as follows. Into exactly 1L of seawater, 0.5 g of Chelex-100 resin and 10 ml of 1M ammonium acetate buffer solution (pH 6) were added. The solution was stirred with a magnetic stirrer for 2 h. The resin was collected on a glass filter and washed with ammonium acetate buffer and pure water. The trace elements adsorbed on the resin were desorbed with 7 ml of 2M HNO_3, and finally the solution was made up to 10 ml with pure water. It was concluded that the batch preconcentration procedure was better than the column one. The batch method required much less time (3 h) than the column method (20 h). Use of a

batch technique for sorption of trace heavy metals on chelate resins was demonstrated in other studies [45-47].

Chakrabarti et al [45] investigated the kinetics of cadmium, lead and copper speciation using Chelex-100 resin and batch technique of sorption. Experiments were done on model solutions containing the metal ions and ions with complexing agents EDTA, NTA and fulvic acid. River water (pH=8.0) and snowmelt (pH=5.6) spiked with a few micrograms per liter of each metal were also used in experiments. The pH of spiked samples was adjusted to 5. After being equilibrated for two days, the spiked samples were filtered through 0.45 μm filter and allowed to stand for one day before kinetics measurements were made. 50-100, 100-200 and 200-400 mesh resin in sodium form was equilibrated with NaOAc-HOAc buffer at pH=5. The resin was kept in buffer solution until the time of experiment. The kinetic behavior of Cu(II) with the 100-200 mesh Chelex resin was only slightly different from that of the 200-400 mesh resin. Both fractions of the Chelex were used for further studies. After sorption under static conditions, metals were eluted from beads with acid and quantified by ICP MS. It was found that the kinetic behavior of metals depends on the nature and concentrations of the complexing agent. For example, less than 10% sorption of metals was observed in 30 min if EDTA/metal ratio exceeded 2.3. NTA showed less of an effect than EDTA on metals sorption. In the presence of an excess of EDTA or NTA, all the investigated metal ions were complexed, forming a slowly dissociated complex. In the presence of fulvic acid, these metals formed complexes with a range of dissociation rates. The results reveal the importance of fulvic acid/metal ion ratio on the lability of complexes formed. Analysis of

a snow sample for Cd, Pb and Cu gave results similar to these for the model solutions of aquo-ions of these metals. Analysis of a river surface water sample showed a significant difference from the model solutions containing metal ions. About 90% of the spiked Pb species was taken up by the Chelex resin in 30 min. The rest of the species were taken up very slowly and were probably strongly bound to humic materials or other polyfunctional complexing agents. At least two kinetically distinguished components of lead were found. Cadmium species were mostly sorbed from river water for 15-20 min and only one kinetically distinguished component of cadmium was found. Sorption of cadmium from model solutions containing Cd(II) and fulvic acid was practically complete in 5 min.

It should be emphasized that experiments were carried out with spiked samples and equilibrium may not have been achieved. Moreover, concentrations of metal ions were 1-2 orders of magnitude higher than in unpolluted natural waters. Benda et al [46] used a 20-fold preconcentration in the batch mode and ICP-AES analysis for determination of PB, Cd and Cu in rainwater. Sorption was carried out on 100-200 mesh Chelex-100 beads at pH=6 for one hour. Afterwards beads were filtered and trace elements eluted by stirring with a small quantity of 1M nitric acid.

Baffi et al. [47] used Chelex-100 (Na-form, 50-100 mesh) and Lewatit TP-207 (H-form, 50 mesh) ion-exchangers under static conditions for speciation and preconcentration of Cr(III), Cu(II) and Mn(II) from seawater. 150 mg of ion-exchange resin was stirred with 300 ml of seawater for 24 hours at pH 6-7. The exchangers were separated by filtration, dried and trace metals eluted by stirring with 2 ml of 1M nitric acid for one hour before GFAAS determination. It was found that Lewatit absorbs more

chromium than Chelex from seawater, apparently because of penetration of a colloidal form into the macroporous Lewatit resin. Only 16% of total chromium was sorbed on Chelex beads from a sea water standard, the rest of the chromium was apparently in the hexavalent or colloidal forms. The authors suggested the use of this batch preconcentration technique for oceanographic cruises.

Sorption under static conditions of Cr(VI) ions from aqueous solutions and natural fresh waters has been investigated and discussed in our previous report [48] and article [49]. It was found that 450 mg portion of Dowex 1-8 anion-exchange resin (100-200 mesh) adsorbed quantitatively 50 ppb of Cr(VI) from 500 ml of fresh water samples. Sulfates at concentrations higher than 200 ppm decreased sorption of Cr(VI) species, while monovalent anions: Cl^-, HCO_3^- and NO_3^- present at concentrations usually found in fresh waters did not suppress Cr(VI) sorption.

Other approaches for speciation and preconcentration of trace metals from water and other samples are the use of ligand-loaded complexing resins, extensively reviewed in the literature [50]. These are obtained by modification of conventional ion-exchange resins and nonionic sorbents with complexing reagents and can be used under static or dynamic conditions. In many cases sorbents modified with chelating reagents demonstrate better selectivity compared with Chelex resin. A problem with ligand-loaded resins is the preparation of a uniform stable product, which can be stored for a long time without changing properties. Currently, these are prepared mostly in the laboratory prior to analytical procedure. This is time-consuming and not practical for routine analysis.

Speciation and preconcentration methods using ligand-loaded resins are not discussed in the present review.

For speciation measurements, in-situ techniques are preferable to minimize analyte losses, contamination, and physicochemical changes during transportation and storage of water samples. In our opinion, a batch resin procedure is more convenient for field speciation and/or preconcentration of trace elements in environmental samples. It can be followed by instrumental analysis in a mobile or stationary laboratory.

2.3.2 GFAAS Determination of Trace Elements in Natural Waters after Preconcentration on Ion-Exchange Resin

The awareness of the effects of trace elements in the environment on human health has fostered the growth of analytical techniques and instrumentation capable of addressing these issues. Accurate and reliable methods of high sensitivity and selectivity are required, applicable to real-world samples, coupled with convenience and economy. GFAAS is one of several such methods of analysis, and has enjoyed widespread application and generated a proven track record of successful activity over the past two decades [35,51]. With the use of stabilized temperature platform furnace and background correction, modern GFAAS has become an accurate method for the determination of trace metals in a wide variety of environmental samples. The method of standard addition is no longer necessary, nor even useful for GFAAS analysis [52].

Significant progress is continuing to be realized in the development of accessory hardware relating to sample introduction and processing. Additionally, complex chemical

processing can be accomplished on-line, often alleviating the need for extensive clean-room facilities. Trace metals are typically preconcentrated on-line using an ion-exchange microcolumn by injection of microliters or milliliters of a sample volumes into a suitable buffered carrier stream and are eluted to the detector by injection of a smaller volume of a mineral acid [10,13,53]. Flame AAS; spectrophotometry and more recently ICP MS are usually used for detection. However, the batch nature of GFAAS precludes its use for routine on-line speciation analysis. On-line couplings can be made but these require the use of either an electrospray or thermospray devices, and even then, running the spectrometer at the atomization temperature for extended periods will lead to rapid tube wear [13].

Despite the high detection power offered by GFAAS, the concentrations of many trace elements in natural water remain below levels amenable to direct analysis and/or matrix components give rise to chemical and spectral interference. Fortunately, preconcentration procedures frequently achieve matrix separation as well. In particular, preconcentration of trace metals in waters using chelate resins allows their separation from the matrix elements. Techniques used off-line are efficient for the separation and concentration of trace elements, yielding preconcentration factors of 100-fold and more. So trace metal concentrations in unpolluted natural waters can be determined. In many cases. The sensitivity is limited by procedural blanks due to impurities introduced from reagents and sample processing.

GFAAS has proven to be a useful method for solids as evidenced by the more than 250 references cited in a review of Benedicto and de Loos-Volleberg [54].

Applications of this technique include various biological samples, plants, food, alloys, soils, rocks, fly ash, plastics, glasses and chemicals. However, direct GFAAS measurements of trace elements sorbed on ion-exchange beads are not covered to any substantial extent in this review.

Advantages of solid sampling compared to conventional sample preparation procedures such as acid digestion include [52,55]: 1) reduced sample preparation time; 2) decreased chance of analyte loss due to volatilization prior to analysis; 3) reduced loss of analyte related to retention by an insoluble residue; 4) reduced possibility of sample contamination; 5) increased sensitivity; 6) less use of hazardous acids. Solids have variable particle size, suggesting possible problems with different atomization efficiencies. However, the furnace uses integration techniques and provides close to 100% atomization efficiency, which minimizes the effect the effect of variable particle size.

A problem with direct solid sampling is poor precision due to manual micro weighing and manipulation with small heterogeneous samples. Slurry sampling has been identified as a good approach, which combines the benefits of solid and liquid sampling [55,56]. Conventional liquid sample-handing devices such as autosamplers and micro pipets may then be used to inject material into the furnace for analysis.

To ensure that a representative aliquot is injected into the furnace, the slurry must be stabilized or homogenized. Sample homogenization using mechanical agitation, vortex mixing, inert gas bubbling and ultrasonic agitation are reviewed and analyzed in the literature [56,57]. Mixing with a compact portable ultrasonic processor provides superior

agitation for slurry preparations. Commercial 40-50 W units designed to process small samples (0.1-25 ml) effectively disperse particles. In addition, ultrasonic agitation can increase the extraction of the analyte into the liquid phase of the slurry. The titanium ultrasonic probe can be mounted on the autosampler tray, providing automated slurry analysis. For slurry preparation a number of diluents have been used, including water, water with addition of surfactants and/or matrix modifiers, and dilute acid solutions. Many researchers recommend dilute nitric acid in order to increase the fraction of analyte in the liquid phase. Accurate results can typically be obtained using as little as 1-5 mg of finely ground sample (<500 μm) suspended in 1 ml of dilute acid. Analysis requires the use of modern furnace technology including platform atomization and Zeeman or Smith-Hieftje background correction. Calibration against aqueous standards provides accurate results with a relative standard deviation of 4-10% [57]. In our opinion fine (<300 μm) ion-exchange beads with sorbed trace elements are ideally suited for slurry sampling and GFAAS analysis. Ion-exchange beads do not need grinding and do not form aggregates in slurry. Their density is typically 1.05-1.15 g/ml and they are more stable in aqueous slurries than suspensions of many other solid materials that have higher density. So, fine ion-exchange beads can be used for preconcentration of trace metals in static conditions and their direct GFAAS determination. Direct GFAAS for the determination of microelements using fine ion exchange beads was first used by Slovak [58]. Isozaki et al. [59] used GFAAS for determination of aluminum sorbed on chelating resin. Ososkov and co-workers applied ion-exchangers for the determination of lead in tap water [60] and for

speciation of chromium in a treated wastewater [61]. These investigations have not been performed on modern GFAAS equipment and standard addition method was used for calibration. Sensitivity and accuracy of analysis were also lower than can be obtained using up to date techniques.

Another option for the determination of trace elements in fine solid samples is a fast quantitative elution of an analyte from beads with a small volume of acid solution and their GFAAS analysis. Minami et al. [62] used extraction with 1M nitric acid, separation on a centrifuge and GFAAS for determination of Cd, Pb, Cu and Mn in biological samples. Nearly 100% extraction of these metals from 50 mg of powdered samples with 5 ml of acid solution was obtained. Relative standard deviation was lower than 4%. This kind of extraction can be tested for GFAAS analysis of trace elements concentrated on ion-exchange resins.

A great deal of experience has been accumulated in selecting furnace time-temperature programs for determination of Pb, Cd and Cr in environmental samples by GFAAS. A serious interference is the formation of volatile compounds. In a graphite furnace, particularly when halides are present, the analyte can be lost as a volatile salt during the ashing or atomization stage at temperatures too low to achieve atomization. In order to avoid volatilization of Pb and Cd and perform the ashing step at higher temperature, matrix modifiers (palladium, lanthanum magnesium nitrates or their mixtures) are typically added to a sample. Sensitivity and accuracy of Cd, Pb, and Cr analysis in waters by GFAAS vary depending on matrix characteristics, equipment used, and parameters of determination. On the basis of literature data and our experience, it can

be concluded that with a reasonable accuracy (5-10% RSD) Cd can be determined in waters at concentrations >0.5 ppb and Pb and Cr at concentrations >1 ppb. Theoretical and practical aspects of trace metals analysis by GFAAS are reviewed in the literature [26,35,63].

On the basis of the literature review it can be concluded that off-line speciation and preconcentration of trace metals occurring in natural waters as cations or weak complexes on Chelex-100 resin followed by GFAAS analysis may be used as a method for their determination. Concentrations of heavy metals in these species are better correlated with their toxicity than concentration of "dissolved" metals after filtration through 0.45 μm membrane. Strong anion-exchange resin can be used for speciation and preconcentration of Cr(VI) in fresh waters. Sorption can be carried out under static conditions on-site in order to avoid transformation of species during transportation and storage. GFAAS determination of trace metals in the concentrate is usually carried out in the laboratory. They can be determined directly in a slurry or after elution with a small quantity of an acid solution. After elution it is also possible to use ICP MS technique for simultaneous determination of many toxic heavy metals (Cd, Pb, Cu, Ni, Zn, etc.) preconcentrated on Chelex resin.

2.4 Speciation of Trace Elements in Sediments

2.4.1. Sequential Speciation Procedures

The total concentration of trace metals in sediments and soil can be determined by standard EPA procedure using acid digestion and spectral analysis [64]. However, these

values alone provide little information of metals mobility, bioavailability, or toxicity. In unpolluted sediments and soils, trace elements like lead and cadmium are mainly bound to silicates and primary minerals forming relatively immobile species, whereas in polluted ones, trace metals are generally more mobile. Sediments consist of many different components and phases, including crystalline minerals, hydrous metal oxides, and organic substances. Trace metals can be bound to particulate matter by several mechanisms such as particle surface adsorption, ion-exchange, coprecipitation, and complexation with organic substances. In environmental studies, the determination of metals bound in different ways gives much more information on trace element mobility, availability and toxicity, in comparison with the total element content. However, the determination of the different binding mechanisms is difficult and often impossible.

Currently, approaches focused on metal desorption from the solid phase are used to evaluate their mobility in sediments and soils. Among these approaches, leaching procedures are the most widely accepted.

Extraction procedures using a single extractant are applied in soil science and are commonly applied in studies of fertility and quality of soils and for predicting the uptake of essential elements by plants. To a lesser extent, they are applied to elements considered as pollutants such as heavy metals. For sediment analysis, extraction is used to evaluate the long term emission potential of pollutants and to study their distribution among different phases of sediments. Single extractants are usually chosen to evaluate a particular release controlling mechanism, such as desorption by increasing acidity, salinity or complexing by competing organic agents. Numerous acid solutions, buffered

and unbuffered salt solutions and chelating agents are proposed, tested and reviewed in the literature [68]. Evidence that exchangeable metals better correlate with plant uptake suggested the use of neutral salts (soft extractants), which mainly solubilize cations sorbed to soil particles by an ion exchange mechanism. Diluted acids partially dissolve trace elements associated with different fractions such as exchangeable, carbonates, iron oxides and organic matter. Complexing agents also extract metals from organic matter complexes. Nowadays, it is generally accepted that extractants are not selective for specific soil or sediment fractions and that minor variations in analytical procedures can have significant effects on the results[67].

Generally, using sequential extraction schemes can isolate soil and sediment fractions more specifically [65]. For sediments, these procedures are frequently used and were originally developed to address problems arising from disposal of dredged sediments. During the last decades, several sequential extraction procedures for extractable heavy metals in soils and sediments have been developed and modified [3,67]. Detailed surveys of these methods, their applications for speciation of trace elements in soil and sediments and the list of relevant literature are presented in recently published books and articles [66,67].

As for soils, exchangeable metals in sediments are selectively displaced by soft extractants. Other extractants used are less selective and they co-extract the exchangeable fraction together with metals bound to other sediment phases, more or less extensively. The phases considered relevant in heavy metal adsorption in sediments are oxides, sulfides and organic matter. The fractions obtained, when applying sequential extraction

schemes, are related to exchangeable metals, metals mostly bound to carbonates, metals released in reducing conditions such as these bound to hydrous oxides of Fe and Mn, metals bonded to oxidizable components such as organic matter and sulfides and a residual fraction. The extractants more commonly used are generally applied in the following order: unbuffered salts, weak acids, reducing agents, oxidizing agents and strong acids.

The most widely used extraction scheme is one proposed by Tessier [3] which several authors have modified [67,70]. These procedures are presented in Table 2.4.

Table 2.4 Three Published Sequential Extraction Schemes [3,67,70]

Method	1	2	3	4	5
Tessier [3]	1M $MgCl_2$ pH 7 Exchangeable	1M NaOAc pH 5 Carbonate	0.04M $NH_2OH.HCl$ 25% HOAc Fe/Mn-oxide	8.8M H_2O_2 HNO_3 / NH_4OAc Organic + sulphide	$HF/HClO_4$ Residual Silicate phase
Forstner [67]	1M NaOAc pH 5 Exchangeable + Carbonate	0.1M $NH_2OH.HCl$ easily reducible	0.1M NH_4O_x/HO_4 pH 3 moderate reducible	8.8M H_2O_2 pH 7, NH_4OAc organic + sulphide	HNO_3 Residual Silicate
Meguelluti [70]	1M $BaCl_2$ pH 7 Exchangeable	8.8M H_2O_2 + HNO_3 Organic + sulphide	1M NaOAc pH 5 Carbonate	0.1M $NH_2OH.HCl$ 25% HOAc Fe/Mn-oxide	Ashing+HF / HCl Residual Silicate

The extraction of the exchangeable fraction uses electrolytes such as salts of strong acids and bases or salts of weak acids and bases at pH=7 to prevent hydroxide precipitation. However, it was demonstrated that the desorption behavior of metal ions

depends on soil-liquid ratio and salt concentration [10]. More labile metals are released within two hours, while others are released over 24 hours.

For extracting the carbonate bound fraction, acetic acid or a buffer solution of acetic acid/sodium acetate at pH=5 is generally used. The extraction is usually completed within 5 hours. These reagents are not able to remove all carbonates. For example, dolomites are extracted only partially. They also partially remove organically bound trace metals [67].

The fraction obtained when a reducing solution is used as extractant is mainly related to metals bound to iron and manganese oxides, which are important components of sediments. Hydroxylamine in acid solution (pH=2) is the reducing agent most widely used to solubilize these oxides although iron oxide is not completely dissolved from some matrixes [73]. The sodium dithionate/citrate/carbonate reagent dissolves the oxide and hydroxides but can attack iron rich silicates. The problem with ammonium oxalate is that some heavy metal oxalates may precipitate even at low pH. This extraction step is usually completed in hours.

Oxidizing reagents have to destroy organic matter and also oxidize sulfides to sulfates. The extractant most widely used in this group is hydrogen peroxide. Sediment samples are boiled with 30% H_2O_2 for several hours.

Strong acids are used for trace metal removal from residual minerals. For complete dissolution of residual silicates acid digestion with $HF/HClO_4$ or $HF/HClO_4/HNO_3$ is used. Special laboratory equipment and safety measures for application of these hazardous mixtures are required. However, in order to extract trace

metals of environmental concern bound to minerals and not included in their crystalline structure, application of hot concentrated NHO_3 or HNO_3/HCl mixture is usually sufficient.

In order to establish common schemes for extractable trace metals in soils and sediments, the European Standards Measurement and Testing Program (ESMTP) has sponsored several projects focused on sequential extraction for soils and sediments. As a result, a sequential extraction scheme was proposed which includes three steps: acetic acid, hydroxylamine hydrochloride as a reducing reagent and hydrogen peroxide as an oxidizing reagent [65]. Moreover, the main analytical limitations in sequential analysis of sediments were discussed and recommendations were given [74,75]. The scheme excludes determination of exchangeable and residual fractions. The ESMTP procedure is presented in Table 2.5.

Table 2.5 European Standard Measurements and Testing Procedure [65]

Step	Conditions
1	0.1M HOAc, 20°C, shaking overnight
2	0.1M $NH_2OH.HCl$ (pH = 2 with HNO_3), 20°C, shaking overnight
3	8.8M H_2O_2 (pH = 2 with HNO_3), room temperature 1 hour, 85°C 1 hour, then use 1M NH_4OAc (pH 2 with HNO_3), 20°C, shaking overnight

The scheme was tested on two types of sediments, siliceous and calcareous. Some critical parameters were identified, such as the type and the speed of the shaking, and the need of uniform separation of the liquid-solid phases after extraction. It was stated that sediment should be continually suspended in the solution during extraction. The next step

of the project was the preparation of a certified reference material for determination of trace metals in sediments. A siliceous type sediment with rather high concentrations of metals was recently certified for Cd, Cr, Ni, Pb and Zn determination [71]. These certified reference materials were not available commercially at the beginning of this investigation in 1996.

A comparative study of different sequential extraction procedures for metals in sediments was performed [72,75]. As expected, the differences found in metal distribution were significant. Usero et. al. compared Tessier [3], Forstner [69] and ESMPT procedures for sequential extraction of Pb, Cr, Zn, Mn, Cu and Fe in marine sediments. The fractions of each method were grouped into four "equivalents" (acid soluble, reducible, oxidable and residual). The Tessier procedure indicated the lowest concentrations of Pb and Cr in acid and oxidable fractions and the highest value of Pb in reducible and residual fractions. Cr was bound more strongly than Pb to sediment particles, with concentrations in the residual fraction of 75-90%. These comparative studies demonstrated that sequential extraction procedures are not connected directly with specific physical-chemical forms of trace metals in sediments and are operationally dependent.

It can be concluded that the advantages of trace metal speciation in sediments over the determination of total metal content are evident. To increase the quality of results, preparation of certified materials and application of detailed universal extraction procedure are beneficial. Nevertheless, some problems remain: reactions are not selective, they are influenced by experimental conditions, and the analytical scheme should be

validated for different types of sediments. Sequential extraction procedure is a time and labor consuming process. It takes 2-3 days to obtain analytical results. In our opinion, development of more rapid and simple speciation schemes (screening methods) is desirable.

2.4.2 Microwave (MCW) Digestion and Speciation of Sediments

MCW digestion is widely used for total trace metals analysis in soil and sediments and is included in the standard EPA procedure [77]. Compared to conventional acid digestion, MCW digestion is much more rapid, and uses a smaller quantity of reagents. The possibility of contamination during sample preparation is also reduced. The theory of MCW digestion procedure [78] and a recent detailed review of its application to digestion of environmental matrixes including sediments [79] is available. However, the application of MCW digestion to sequential extraction is not mentioned in these sources.

To our knowledge, the only study of MCW technique for sequential extraction of trace elements was published by Campos et al in 1998 for calcareous soils [80]. Analysis of Pb, Zn and Cu in four fractions after a sequential extraction procedure was performed. The analytical procedure for partitioning trace metals into the following forms was performed: 1). Carbonate bound+Exchangeable+Water soluble. 2). Fe/Mn oxide bound. 3). Organic matter bound. 4). Residual. The exchangeable fraction with $MgCl_2$ was dropped because no released metals were detected. MCW heating was set up in such a way that the sample did not boil over, or result in very dry residue. To optimize the extraction procedure, the leaching of Ca (step 1), and Fe and Mn (step 2) were

investigated for several heating times. Concentrations of Al and Si in different fractions were also measured to find out if the decomposition of silicates occurred. The content of trace metals in different fractions was determined by flame AAS after centrifugation. The microwave sequential extraction procedures [80] are given in Table2.6.

Table 2.6 Microwave Sequential Extraction by Campos et al [80]

- 1 g of soil+20 ml NaOAc 1M at pH 5, microwave for 5 min at 50% power
  Dilute to 20 ml with water and centrifuge for Carbonate bound metals (F1)
- Extraction with 20 ml $NH_2OH.HCl$ 0.072M in AcOH 4.25M
  Microwave 30 min at 25% power
  Dilution to 20 ml with water and centrifuge for metals bound to Fe/Mn-oxide (F2)
- Twice extraction with 3.5 ml HNO_3 0.02M+5 ml H_2O_2 30% microwave to near dryness 50% power and 75% power respectively. Add 5 ml NH_4Ac 3.2M in HNO_3 3.2 M.
  Dilution to 20 ml with water and centrifuge for Organic bound fraction (F3)
- Extraction with $HClO_4$+HF, Tessier method
  Dilute to 25 ml with HCl 1M for residual fraction (F4)

Precision of the procedure was checked on parallel samples for different extraction steps. Generally, the RSD does not exceed 10%. Accuracy of the method could not be evaluated with the reference material. The sum of the Pb, Zn and Cu found in different fractions was close (7-12%) both to the certified values and the total concentrations determined experimentally. An important advantage is that proposed MCW sequential extraction requires only two hours and is much faster than the conventional extraction procedure.

It is evident that sequential extraction of trace metals from soil and sediments using MCW digestion may be useful for rapid evaluation of their environmental properties. More experiments are necessary with different types of sediments, metals, and experimental conditions to evaluate advantages and limitations of MCW application for sequential extraction procedures. In our opinion, it would be interesting to compare MCW digestion with the conventional sequential extraction procedure using the same reagents. In 1997, we started an investigation of MCW sequential extraction for determination of Pb, Cd and Cr in different fractions of several sediment samples.

CHAPTER 3

OBJECTIVE

A primary objective of this work was the development of an improved method for determination of trace metals by preconcentration by adsorption on ion exchange resin and then determination of these metals, Cd, Pb, Cr(III),Cr(VI), in natural waters by GFAAS and/or ICP-MS. The natural waters here include river water, lake water, drinking water, and seawater. The current EPA method for the determination of total dissolved metals includes complexed and colloidal forms. This research work will focus on the free ions. Both the EPA method and the proposed method will be used in this study for obtaining information on the fraction of the metals present in bound and free forms.

The ion exchange resins used here for preconcentration of the metals in waters are Chelex 100 resin for cation exchange, and Dowex 1x8 resin for anion exchange. Initial work was done using synthetic samples prepared in ultrapure distilled water. Instrument operating conditions for GFAAS, including the temperature program were developed. After the methods were optimized, various water samples were analyzed for the metals of interest. The acceptable sample storage times, kinetics of metals sorption, a comparison of supernatant injection with slurry injection, the recovery of spiked samples, Pd matrix modifier were studied. The standard deviation, relative standard deviation, accuracy, reproducibility, and detection limit of the method were determined.

A second objective was the development of a more rapid method to speciate the target metals in sediments. Sample preparation by the conventional stirred batch sequential

extraction procedure is a lengthy procedure. The proposed method, using microwave extraction was designed to give similar information in a much shorter time.

An analytical method including the sequential extraction of the metals of interest from the sediment samples and the operating conditions for analysis of the metals by GFAAS was developed. Sediment samples from Newark Bay, and Shark River, Atlantic City Bay were analyzed. A Modified Tessier Method (MTM), Microwave Method (MWM), and standard EPA method were used in this research, and the data from each method were compared.

A study of the kinetics of the sequential extraction procedure with selective extractants was carried out. Effects of temperature and pressure on the microwave digestion of the sediments was investigated. Comparison of 1M NH_4OAc and 4.5M NH_4Oac for extraction of exchangeable metals by microwave technique was also studied.

The final section of the project applied the methods developed to a group of water, sediment and biota samples.

CHAPTER 4

METHOD DEVELOPMENT AND VALIDATION FOR PRECONCENTRATION, SPECIATION, AND DETERIMNATION OF DISSOLVED HEAVY METALS IN WATER

4.1 Experimental

4.1.1 Equipment

The atomic absorbance spectrometer used in this work was supplied by Thermo Jarrell Ash, equipped with a graphite furnace atomizer, model 188, with Smith-Hieftje background correction capability. It is a dual channel, double beam spectrometer, using diffraction grating monochromator. The bandwith can be adjusted from 0.04 to 2.0, and wavelengths between 190 nm and 800 nm, may be used. A photomultiplier detector is used. Hollow cathode lamps for Cd, Cr, and Pb were used in this research.

In order to stabilize the atomization temperature, the pyrolytically coated graphite furnace tubes used were equipped with a solid pyrolytic graphite L'vov platform. The graphite furnace tubes were purchased from CPI, Inc.

The VG Plasmaquad II was used for water sample analysis. This inductively coupled plasma-mass spectrometer enables simultaneous multi-element analysis. The instrument consists of a plasma torch, a quadrupole mass spectrometer, and a water-cooled plasma interface. The function of interface is to transfer a sample of the ions formed in the plasma into the mass spectrometer's high vacuum chamber. The sample introduction system consists of a peristaltic pump, a nebulizer, and a spray chamber.

4.1.2 GFAAS Operating Condition

1. Hollow Cathode Lamps for Pb, Cd, and Cr.

2. Water flow at 15 GPH

3. Compressed air at 58 psi.

4. Argon at 58 psi.

4.1.2.1 Instrument Condition for Pb

1. Wavelength at 217 nm

2. High voltage at 700

3. Monochromator slit width is 1.0 nm

4. Background current is 2.5 mA

5. Signal current is 5.0 mA

4.1.2.2 The Optimized Furnace Program for Pb

	Drying	Pyrolysis I	Pyrolysis II	Atomization	Cleaning
Temp.(°C)	110	300	490	1800	2550
Ramp(°C/sec)	10	10	20	0	
Hold(sec)	5	5	15	4	4
Purge	1	2	3	0	3

4.1.2.3 The Standard Calibration Curve for Pb

PPB	Abs.
0.0	0.0
2.0	0.020
5.0	0.055
10.0	0.106
20.0	0.210

Correlation = 0.99988

4.1.2.4 Instrument Conditions for Cr

1. Wavelength at 357.9 nm

2. High voltage at 460

3. Monochromator slit width is 1.0 nm

4. Background current is 2.5 mA

5. Signal current is 4.8 mA

4.1.2.5 The Optimized Furnace Program for Cr

	Drying	Pyrolysis I	Pyrolysis II	Atomization	Cleaning
Temp.(°C)	200	800	800	2150	2500
Ramp(°C/sec)	15	15	15	0	
Hold(sec)	0	0	0	4	2
Purge	1	2	2	0	3

4.1.2.6 The Standard Calibration Curve for Cr

PPB	Abs.
0.0	0.0
2.5	0.02
6.0	0.048
12.0	0.096
24.0	0.196

Correlation = 0.9999

4.1.2.7 Instrument Conditions for Cd

1. Wavelength at 228.8 nm

2. High voltage at 700

3. Monochromator slit width is 1.0 nm

4. Background current is 2.5 mA

5. Signal current is 3.0 mA

4.1.2.8 The Optimized Furnace Program for Cd

	Drying	Pyrolysis I	Pyrolysis II	Atomization	Cleaning
Temp.(°C)	150	200	250	1400	2200
Ramp(°C/sec)	2	10	10	0	
Hold(sec)	0	0	0	4	3
Purge	1	2	1	0	3

4.1.2.9 The Standard Calibration Curve for Cd

PPB	Abs.
0.0	0.0
0.03125	0.020
0.625	0.039
1.25	0.086
2.50	0.186
5.00	0.321

Correlation = 0.99666

4.1.2.10 ICP/MS Instrument Operations:

Instrument VG PlasmaQuad Type II

Plasma forward power 950W

Coolant flow rate 12.5 l/min

Auxiliary flow rate 0.75 l/min

Nebulizer flow rate 0.702 l/min

Internal standards Sc, Y, In, Bi

Data Acquisition

Detector mode Pulse counting

Mass range 6 - 240 amu

Dwell time 320 us

Channels/amu 20

Time/Sweep (1.33 sec)(60 sec) = 79.8 sweeps

4.2 Reagents

- Ultrapure deionized water: DI water is passed through a mixed bed of anion and cation exchange resin. It is used for the preparation of the blanks, standards and as dilution water.

- Nitric Acid (concentrated): Spectrograde (Fisher Chemical, Fisher Scientific)

- Nitric Acid (5%)(v/v): 50 ml concentrated nitric acid diluted to 1000 ml with ultrapure DI water.

- Nitric Acid (1%)(v/v): 10 ml concentrated nitric acid diluted to 1000 ml with ultrapure DI water.

- Hydrochloric Acid (concentrated)

- Glacial Acetic Acid

- pH 5 buffer solution: 200 ml ultrapure water, mix with 12 ml Acetic Acid, and 1 M NaOH

- Hydrogen Peroxide 30%: Reagent grade. (Fisher Chemical, Fisher Scientific)

- Standards used for GFAAS: purchased from Fisher Scientific and Aldrich, then diluted with 5% nitric acid.

- Multielement Standard Stock Solution for ICP/MS: purchased from J.T. Baker.

- Calibration Standard Solution for ICP/MS: multielement standard solution diluted to cover the operating range using 1%(v/v) nitric acid

- Multielement Internal Standard Solution for ICP/MS: purchased from J.T.Baker.

- Blanks: 1% (v/v) nitric acid

- pH buffer solution, pH 4,7,10 (Thomas Scientific Inc.): used for pH meter calibration

- Chelex-100: 100-200 mesh, Na(+) form (Bio-rad Laboratories)

- Dowex 1x8: 100-200 mesh, chloride form (Bio-rad Laboratories)

4.3 Apparatus and Supplies

- Analytical balance: sensitivity 0.1 mg
- assorted pipets
- Filters: 0.2 um and 0.45 um (Whatman cellulose nitrate membrane)
- filter holders
- Argon (Matheson Gas Products inc.)
- Test tubes: made of polypropylene (American Scientific Products Inc. and Becton Dickinson Labware Company)

4.4 Cleaning of Apparatus

In order to avoid contamination, storage bottles, sampling containers, pipettes, filtration apparatus, polypropylene beakers were thoroughly washed with nitric acid (1:1), deionized water, hydrochloric acid (1:1), DI water, and then rinsed with ultrapure deionized water.

4.5 Experimental Procedure

Initial work was done using synthetic samples prepared in ultrapure distilled water. Instrument operating conditions for GFAAS which includes the furnace temperature program, and for ICP-MS, were developed. Lead, cadmium, and chromium were analyzed. Natural water samples were also spiked to determine interferences and recovery.

The water samples were collected in the field. Half of the sample was filtered into a plastic container through a 0.45 um filter membrane immediately, as is done for the current EPA method for total dissolved metals analysis. The rest of the sample was

acidified to a pH below 2 with an ultrapure concentrated nitric acid in a plastic container for total metals analysis and for storage studies.

The adsorption efficiency and the time required for quantitative sorption are functions of pH, ion exchange resin used, the ratio of the amount of ion exchange resin to the volume of water samples, and the stirring rates. All of these parameters were studied.

After the methods were optimized, various water samples were analyzed for the metals of interest. Storage period, standard deviation, relative standard deviation, accuracy, reproducibility, detection limit of the method were determined.

4.5.1 Speciation of Trace Metals Cd, Cr, Pb

4.5.1.1 Determination of Total Metals in Water, EPA Method: The fresh water sample was acidified with ultrapure concentrated nitric acid to a pH of less than 2 before storage. For analysis, 250 ml of sample was transferred to a Griffin beaker. 3 ml of concentrated nitric acid was added. The sample was then heated on a hot plate and evaporated to near dryness without boiling. After cooling, 3 ml of concentrated nitric acid was added to the sample. The beaker, covered with a watch glass, was returned to the hot plate.

The temperature was adjusted to create a gentle reflux action, until the digestion was complete. The sample was then evaporated to near dryness and cooled. A small amount of nitric acid (1:1) was added and the sample was warmed to dissolve the residue or precipitate. The watch glass and beaker wall were washed with ultrapure DI water. The sample was mixed well, then filtered to remove any insoluble material.

The sample was then evaporated to less than 3 ml, and transferred to a 10 ml test tube and diluted to 5 ml with 1% nitric acid. The sample then was ready for analysis.

4.5.1.2 Determination of Dissolved Cd, Cr, Pb in Water, EPA Method: A fresh sample was filtered through a 0.45 um membrane filter. 250 ml filtered water was acidified to a pH less then 2 with concentrated nitric acid. The sample was evaporated to a volume less than 3 ml on a steam bath, and then 1% nitric acid was added to the volume desired. The sample was ready for analysis.

4.5.1.3 Determination of the Exchangeable Cd, Cr(III), Pb, Cr(VI): A water sample was filtered through a 0.45 um membrane filter immediately after collection. 250 ml filtered water, 0.25g Chelex-100, and 5 ml pH5 buffering solution was added into a polypropylene beaker. The sorption process was continued for 3 hours under magnetic stirring. The Chelex resin was filtered and then washed off the filter with a 3% nitric acid into a test tube. The sample was ready for analysis.

For Cr(VI): The procedure is the same as above, except Dowex 1x8 was used rather than Chelex 100 and the buffer was omitted.

4.6 Results and Discussion

4.6.1 Kinetics of Sorption of Cd and Cr(VI) on Ion Exchange Resins

Better than 80% of each analyte was sorbed on Chelex 100 and Dowex 1x8 within half an hour, and within two hours, the sorption reached 98%.

(1) Cadmium Sorption

A 0.25 g portion of Chelex 100 was added to each of five 250 ml portions of 0.2 ppb standard Cd solution, with 5 ml pH 5 buffer. The samples were stirred for 0.5 hr, 1 hr, 2 hr, 3 hr, and 24 hrs. These five solutions were filtered through 0.45 um membrane filters at the end of the sorption time. The Chelex 100 resin was washed off the filters with 5 ml of 5% nitric acid solution into a plastic test tubes (Table 4.1 and Figure 4.1).

Table 4.1 Kinetics of sorption of Cd on Chelex 100

Contact time (Hr)	Actual(ppb)	Experimental(ppb)	Extraction Efficiency(%)
0.5	0.2	0.168	84.00
1	0.2	0.1804	90.20
2	0.2	0.1962	98.04
3	0.2	0.19664	98.34
24	0.2	0.1976	98.80

(2) Cr(VI) Sorption

Six 0.25 g portions of Dowex 1x8 were added to six 250 ml portions of 0.8 PPB standard Cr solutions. The samples were stirred for 0.5 hr, 1 hr, 2 hr, 3 hr, 4.5 hr, and 24 hrs. These six solutions were filtered through 0.45 um membrane filter at the end of the sorption time. The Dowex 1x8 resin was washed off the filter with 5 ml of 5% nitric acid solution into a plastic test tube (Table 4.2 and Figure 4.2).

4.6.2 Comparison of Supernatant Injection with Slurry Injection for Cr(VI)

When the slurry of ion exchange beads in 5% nitric acid was shaken for two minutes, and allowed to settle, it was found that the acid contained all the analyte. The concentration of acid was varied and it was found that the results were low if the acid content was below 1%. All succeeding experiments were done in 5% acid, both for the slurry and the supernatant methods. A 20 ul aliquot of the supernatant solution was taken for analysis. A series of Cr(VI) standards were run at different concentrations by preconcentration of the Cr(VI) from prepared samples with Dowex resin, and elution with 5% nitric acid. The supernatant solution was analyzed.

Table 4.2 Kinetics of sorption of Cr(VI) on Dowex1x8

Contact time (Hr)	Actual(ppb)	Experimental(ppb)	Extraction Efficiency(%)
0.5	0.8	0.6900	86.25
1	0.8	0.7287	91.09
2	0.8	0.7860	98.26
3	0.8	0.7867	98.35
4.5	0.8	0.7888	98.60
24	0.8	0.7910	98.88

This same set of Cr(VI) standards were also analyzed as slurries. The data from supernatant injection showed better accuracy and reproducibility than injection as slurries.

Since the slurry of ion exchange resin was shaken for 2 minutes, and the slurry began to settle as soon as shaking ceased, the operator's skill is important to obtain a reproducible injection of slurry. For these reasons, the work was carried out using the injection of supernatant (Table 4.3 and Figure 4.3).

Table 4.3 Comparison of slurry and supernatant Analysis methods on Cr(VI)

Actual (ppb)	Slurry(Efficiency)	Supernatant(Efficiency)
0.2	0.1838 (91.90%)	0.195 (97.50%)
0.4	0.3526 (88.15%)	0.3902(97.55%)
0.8	0.78864(98.58%)	0.7865(98.32%)
1.0	0.89355(89.36%)	0.9824(98.24%)

4.6.3 Storage Study

It is inherently not easy to store water samples, as they are prone to chemical change with time. They are bulky and heavy, and need refrigeration. When the metals in water samples are speciated and preconcentrated on the appropriate ion exchange resins, the resulting metal-loaded resins are compact, stable, and easy to store for long periods of time. Samples intended for archival purpose, or those which do not need to be immediately analyzed, can be stored on the ion exchange resin. The resin is filtered from sample, and the dry resin beads can be stored. In a sample which has already been analyzed, and is needed for future analysis or for archival purposes, the beads can be

stored in the 5% nitric acid solution, after a portion has been removed for slurry or acid solution analysis.

Standard solutions were sorbed and the resin beads stored both wet and dry, and analyzed after 3 weeks and 5 months of storage (Figure 4.4, 4.5,4.6).

4.6.3.1 Three Weeks Dry and Wet Storage Studies on Lead

1) Dry Sample

Three 0.25 g portions of Chelex 100 were added to 250 ml of 0.2 PPB, 0.8 PPB, and 1.0 PPB standard Pb solutions, mixed with 5 ml pH 5 buffer solution. The solution was stirred slowly for 3 hours, and then poured through a 0.45 um membrane filter. The Chelex 100 resin was collected and stored in a 4 ° C cold room for 3 weeks (Table 4.4).

Table 4.4 Three weeks dry storage study on Pb

Actual (ppb)	Experimental (ppb)	Recovery(%)
0.2	0.197	98.35
0.8	0.785	98.13
1.0	0.982	98.15

2) Wet sample

Three 0.25 g portions of Chelex 100 were added to 250 ml of 0.2 PPB, 0.8 PPB, and 1.0 PPB standard Pb solutions, mixed with 5 ml pH 5 buffer solution. The solution was stirred slowly for 3 hours, and then poured through a 0.45 um membrane filter. The Chelex 100

resin was washed off the filter with 5 ml 5% nitric acid solution into a plastic test tube, and stored in a 4 ° C cold room for 3 weeks (Table 4.5).

Table 4.5 Three weeks wet storage study on Pb

Actual (ppb)	Experimental (ppb)	Recovery(%)
0.2	0.197	98.30
0.8	0.785	98.10
1.0	0.983	98.27

4.6.3.2 Three Weeks Dry and Wet Storage Studies on Cd: Same procedure as for Pb was used (Table 4.6, 4.7).

Table 4.6 Three weeks dry storage study on Cd

Actual (ppb)	Experimental (ppb)	Recovery(%)
0.2	0.1967	98.38
0.4	0.3934	98.37
0.8	0.7865	98.32
1.0	0.9843	98.43

4.6.3.3 Three Weeks Dry and Wet Storage Studies on Cr(VI): Same procedure as for Pb, except without pH 5 buffer solution, and using Dowex 1x8 instead of Chelex 100 (Table 4.8, 4.9).

Table 4.7 Three weeks wet storage study on Cd

Actual (ppb)	Experimental (ppb)	Recovery(%)
0.2	0.197	98.30
0.4	0.394	98.55
0.8	0.787	98.38
1.0	0.983	98.34

Table 4.8 Three weeks dry storage study on Cr(VI)

Actual (ppb)	Experimental (ppb)	Recovery(%)
0.2	0.1963	98.17
0.4	0.3926	98.15
0.8	0.7862	98.28
1.0	0.9836	98.36

Table 4.9 Three weeks wet storage study on Cr(VI)

Actual (ppb)	Experimental (ppb)	Recovery(%)
0.2	0.1950	97.50
0.4	0.3900	97.50
0.8	0.7865	98.32
1.0	0.9824	98.24

4.6.3.4 Five Months Dry and Wet Storage Studies on Cd, Cr(VI), Pb: Time period: Feb. 26, 1998 -- July 22, 1998 (Table 4.10 and Figure 4.7)

Table 4.10 Five months dry and wet storage on Cd, Cr and Pb

Cd	Actual (ppb)	Experimental (ppb)	Recovery(%)
Dry sample	0.2	0.1964	98.20
Wet sample	0.2	0.1965	98.25
Cr(VI)	Actual (ppb)	Experimental (ppb)	Recovery(%)
Dry sample	0.8	0.7843	98.02
Wet sample	0.8	0.7834	97.93
Pb	Actual (ppb)	Experimental (ppb)	Recovery(%)
Dry sample	0.8	0.784	98.00
Wet sample	0.8	0.7848	98.10

4.7 Field Samples

In order to test the effects of various types of natural waters, a variety of field samples were collected from bodies of water in New Jersey, and then analyzed. The natural water includes river water, tap water, lake water, and seawater. River water samples were taken from the Passaic River between Kearny and North Arlington. Tap water was collected at Newark. A

lake water sample was taken from Parsippany Lake in Parsippany, and a seawater sample was collected at Sandy Hook. Each of these samples was collected in a 4 liter plastic bottle. Half of each sample was analyzed immediately, and the remainder was stored in the 4 ° C cold room for archival purposes.

These samples were analyzed for total metals, dissolved metals, and exchangeable metals for comparison. Spiked samples were also done to determine if any naturally occurring colloidal substances or complexing materials which might be present in the waters would have an effect on the sorption process.

4.8 Quality Assurance

4.8.1 Blank Studies on Milli-Q Water Used in Analyses

Recovery was determined from a known standard solution spiked into the sample of interest. EPA defines the recovery as follows:

$$\% \text{ Recovery} = 100 (X_s - X_u) / K$$

Where:

X_s: measured concentration for the spiked sample

K: known concentration of the spike in the sample

X_u: Measured concentration of the unspiked sample

Contamination of Milli-Q water from ATC building in NJIT was measured using Chelex 100 (for Cd, Pb) and Dowex 1x8 (for Cr(VI)) preconcentration procedure. The

Milli-Q water samples were then spiked with 0.2 ppb Cd, 0.4 ppb Pb, and 0.8 ppb Cr standard solution (Figure 4.8). The metals concentration in the Milli-Q water was below the detection limit. Each metal was done with three replicates, and a minimum 98% recovery for each metal was achieved. The results are presented in Table 4.11.

Table 4.11 Recovery study for Cd, Pb, Cr(VI)

(1) Spike 0.2 ppb Cd

	1	2	3	Mean	SD	%RSD
Milli-Q H_2O (Blank)	ND*	ND	ND			
Actual	0.2	0.2	0.2	0.2		
Experimental	0.196	0.196	0.197	0.196	0.0006	0.31

%Recovery for Cd = 100(0.196 - 0.0)/0.2 = 98.0

* : Non detectable

(2) Spike 0.4 ppb Pb

	1	2	3	Mean	SD	%RSD
Milli-Q H_2O (Blank)	ND	ND	ND			
Actual	0.4	0.4	0.4	0.4		
Experimental	0.394	0.392	0.393	0.393	0.001	0.25

%Recovery for Pb = 100(0.393 - 0.0)/0.4 = 98.25

Table 4.11 (continued)

(3) Spike 0.8 ppb Cr(VI)

	1	2	3	Mean	SD	%RSD
Milli-Q H_2O (Blank)	ND	ND	ND			
Actual	0.8	0.8	0.8	0.8		
Experimental	0.784	0.785	0.786	0.785	0.001	0.13

%Recovery for Pb = 100(0.785 - 0.0)/0.8 = 98.13

4.8.2 GFAAS Instrument Detection Limit, Method Detection Limit and Minimum Detection Level (ppb) for Cd, Cr, and Pb

4.8.2.1 Instrument Detection Limit: The Scientific Apparatus Makers Association (SAMA) defines Instrument Detection Limit as:

$$S_m = X_{bl} + 3S_{bl}$$

Where:

S_m: Detection Limit

X_{bl}: mean of blank

S_{bl}: standard deviation of blank

Blanks were prepared from ultrapure deionized water, buffered at pH 5 and treated with the Chelex 100 resin for Cd, and Pb. Blanks without buffer solution were treated with Dowex 1x8 for Cr(VI). Five replicates were done for this work.

4.8.2.2 Method Detection Limit: The minimum concentration of the sample which can be determined with a 99% confidence.

1) Cd

The method detection limit for Cd is 0.0075 ppb. 0.25 g of Chelex 100 were added to 250 ml of 0.0075 ppb standard Cd solution, with 5 ml of pH 5 buffer solution. The solution was stirred slowly for 3 hours. The Chelex 100 resin was washed off and eluted in 5 ml of nitric acid. This yields a 0.375 ppb concentration of Cd in the 5 ml solution which is easily determined by GFAA. This is a concentration factor of 50. The lowest standard used for the standard calibration curve was 0.3125 ppb. The 0.375 ppb Cd sample is within the standard calibration range (Table 4.12).

Table 4.12 Method detection limit on Cd

	1	2	3	Mean	SD	%RSD
Milli-Q H_2O (Blank)	ND	ND	ND			
Actual (ppb)	0.375	0.375	0.375	0.375		
Experimental (ppb)	0.367	0.367	0.369	0.368	0.0012	0.33

% Efficiency = 100 (0.368 / 0.375) = 98.13

2) Pb

The method detection limit for Pb is 0.04 ppb. 0.25 g of Chelex 100 were added to 250 ml of 0.04 ppb standard Cd solution, with 5 ml of pH 5 buffer solution. The solution was stirred slowly for 3 hours. The Chelex 100 resin was washed off and concentrated to 5 ml. This yields a 2.0 ppb concentration of Pb in the 5 ml solution which is easily determined by

GFAA. This is a concentration factor of 50. The lowest standard used for the standard calibration curve was 2.0 ppb. The 2.0 ppb Pb sample is within the standard calibration range (Table 4.13).

3) Cr(VI)

The method detection limit for Cr(VI) is 0.05 ppb. 0.25 g of Dowex 1x8 were added to 250 ml of 0.05 ppb standard Cr solution. The solution was stirred slowly for 3 hours. The Dowex 1x8 resin was washed off and concentrated to 5 ml. This yields a 2.5 ppb concentration of Cr in the 5 ml solution which is easily determined by GFAA. This is a concentration factor of 50. The lowest standard used for the standard calibration curve was 2.5 ppb. The 2.5 ppb Cr(VI) sample is within the standard calibration range (Table 4.14).

Table 4.13 Method detection limit on Pb

	1	2	3	Mean	SD	%RSD
Milli-Q H_2O (Blank)	ND	ND	ND			
Actual (ppb)	2.0	2.0	2.0	2.0		
Experimental (ppb)	1.96	1.96	1.97	1.96	0.006	0.31

% Efficiency = 100 (1.96 / 2.0) = 98.0

Table 4.14 Method detection limit on Cr(VI)

	1	2	3	Mean	SD	%RSD
Milli-Q H_2O (Blank)	ND	ND	ND			
Actual (ppb)	2.5	2.5	2.5	2.5		
Experimental (ppb)	2.44	2.45	2.46	2.45	0.01	0.41

% Efficiency = 100 (2.45 / 2.5) = 98.0

4.8.2.3 Minimum Detection Level: The lowest level which the analyte can give a recognizable signal and an acceptable calibration point.

Minimum Detection Level = 3.18 x method detection limit

Cd = 3.18 x 0.0008 = 0.025 ppb

Pb = 3.18 x 0.04 = 0.127 ppb

Cr(VI) = 3.18 x 0.05 = 0.159 ppb

4.9 Determination of Trace Metals Cd, Cr, and Pb in Passaic River Water Samples, Samples were collected on Oct.20, 1996 between N. Arlington and Kearny, NJ.

The Passaic River water samples were prepared using the EPA method for the determination of the total metals and dissolved metals, and by the ion exchange bead sorption method using Chelex 100 resin for Cd, Pb,and Cr(III), and Dowex 1x8 resin for Cr(VI) (Figure 4.9). Three replicates were done for each method. The dissolved metal method and the sorption method gave very similar results, indicating that more than 90% of the dissolved metals is exchangeable (Table 4.15).

Table 4.15 Total, dissolved, and exchangeable Cd, Pb, Cr in Passaic River water

(1) Cd (Unit: ppb)

	1	2	3	Mean	SD	%RSD
Total Cd	0.179	0.183	0.19	0.184	0.006	3.26
Dissolved	0.023	0.023	0.026	0.024	0.0017	7.08
Exchange	0.022	0.023	0.024	0.023	0.001	4.35

Table 4.15 (continued)

(2) Pb (Unit: ppb)

	1	2	3	Mean	SD	%RSD
Total Pb	15.01	15.20	15.48	15.23	0.236	1.55
Dissolved	1.56	1.58	1.63	1.59	0.036	2.26
Exchange	1.46	1.47	1.51	1.48	0.026	1.76

(3) Cr (Unit: ppb)

	1	2	3	Mean	SD	%RSD
Total Cr	6.41	6.65	6.86	6.64	0.225	3.39
Dissolved Cr	0.96	0.99	1.08	1.01	0.062	6.14
Exchange Cr(VI)	0.70	0.73	0.79	0.74	0.046	6.22
Exchange Cr(III)	0.20	0.21	0.22	0.21	0.010	4.76

4.10 Determination and Spike Study of the Trace Metals Cd, Cr, and Pb in Parsippany Lake Water Samples. Samples Were Collected on January 05, 1997 at Parsippany, NJ.

4.10.1 Determination of Cd, Cr(III), Cr(VI), Pb in Parsippany Lake Water Sample

The Parsippany Lake water samples were prepared using the EPA method for the determination of the total metals and dissolved metals, and by the ion exchange sorption method using Chelex 100 resin for Cd, Pb, and Cr(III), and Dowex 1x8 resin for Cr(VI). A spike study was also done with the sorption method to verify the developed method. The results are presented in Table 4.16 and Table 4.10.

Table 4.16 Total, dissolved, and exchangeable Cd, Pb, Cr(VI), Cr(III) in Parsippany Lake water, unit: ppb

(1) Cd

	1	2	3	Mean	SD	%RSD
Total Cd	0.031	0.032	0.036	0.033	0.0026	7.88
Dissolved	0.023	0.025	0.027	0.025	0.002	8.08
Exchange	0.023	0.023	0.026	0.024	0.0017	7.08

(2) Pb

	1	2	3	Mean	SD	%RSD
Total Pb	0.81	0.86	0.88	0.85	0.036	4.24
Dissolved	0.278	0.284	0.287	0.283	0.0046	1.63
Exchange	0.271	0.280	0.283	0.278	0.006	2.16

(3) Cr

	1	2	3	Mean	SD	%RSD
Total Cr	0.21	0.24	0.24	0.23	0.017	7.39
Dissolved Cr	0.17	0.18	0.19	0.18	0.01	5.56
Exchange Cr(VI)	0.11	0.12	0.13	0.12	0.01	8.33
Exchange Cr(III)	0.042	0.045	0.05	0.046	0.004	8.70

The data are nearly identical between dissolved metals by EPA method and metals sorbed by ion exchange resin. It is clear that almost all the dissolved metals are exchangeable.

4.10.2 Spike Study on Parsippany Lake Water

After the determination of Cd, Cr, and Pb in Parsippany Lake water, the water sample was used for a spike study.

Chelex 100 (for Cd, Pb) and Dowex 1x8 (for Cr(VI)) preconcentration procedure was used in the spike study. The water samples were spiked with 0.02 ppb Cd, 0.2 ppb Pb, and 0.1 ppb Cr(VI) standard solution. The recoveries of each of the metal ions was at least 98% for three replicates. The results are presented in Table 4.17.

Table 4.17 Spike study on Parsippany Lake water for Cd, Cr, Pb

(1) Spike 0.02 ppb Cd

	1	2	3	Mean	SD	%RSD
Lake H_2O	0.024	0.024	0.024	0.024		
Actual	0.044	0.044	0.044	0.044		
Experimental	0.043	0.044	0.044	0.0436	0.0006	1.38

%Recovery for Cd = 100(0.0436 - 0.024)/0.02 = 98.0

(2) Spike 0.2 ppb Pb

	1	2	3	Mean	SD	%RSD
Lake H_2O	0.278	0.278	0.278	0.278		
Actual	0.478	0.478	0.478	0.478		
Experimental	0.474	0.474	0.475	0.4743	0.0006	0.13

%Recovery for Pb = 100(0.4743 - 0.278)/0.2 = 98.15

Table 4.17 (continued)

(3) Spike 0.1 ppb Cr(VI)

	1	2	3	Mean	SD	%RSD
Lake H_2O	0.12	0.12	0.12	0.12		
Actual Cr(VI)	0.22	0.22	0.22	0.22		
Experimental	0.217	0.218	0.219	0.218	0.001	0.46

%Recovery for Pb = 100(0.218 - 0.12)/0.1 = 98.00

4.11 Pd Matrix Modifier Test

For some of the experiments on lead and cadmium which were done on slurried samples, a palladium nitrate modifier, $Pd(NO_3)_2$, was added to the graphite furnace with the sample. This was an attempt to stabilize the analyte and reduce losses in the pyrolysis step. 1% palladium nitrate modifier was used. The data were compared with similar samples done without the modifier, under the optimized instrument conditions described above, and little difference was found, although a higher atomization temperature (600 - 1000 °C) was required with the modifier. The results indicated that there was no advantage in this method for these metals. Since the reagent is expensive, and involves an additional step in the analysis, and significant improvement was not found, it was not used in further experiments.

Expt. 1) Pd was mixed with 10 ppb Pb slurry solution, then the supernatant of the slurry solution was analyzed by GFAAS.

The absorbance reading were:

0.069, 0.058, 0.068, 0.060, 0.063, 0.066, 0.055

mean = 0.0627, SD = 0.0053, %RSD = 8.45

Expt. 2) Another 10 ppb Pb slurry solution without added Pd modifier was also analyzed by GFAAS. The absorbance reading were:

0.083, 0.086, 0.093, 0.085, 0.081, 0.083, 0.091

mean = 0.0860, SD = 0.0044, %RSD = 5.12

4.12 Speciation and Determination of Trace Metals Cd, Cr(VI), Pb in Drinking Water, and Parsippany Lake Water, NJ, by ICP/MS

ICP/MS is significantly more expensive than GFAAS, and it also requires more operator skill, and is more complicated to maintain. It has an advantage over the GFAAS in that it can determine all the metals simultaneously.

The precision and accuracy of the method were determined. The detection limit for Cd was found to be 0.0075 ppb, 0.04 ppb for Pb, and 0.05 ppb for Cr(VI) with the ion exchange resin method. The recovery study on the spiked samples by ICP/MS were similar those found in the study by GFAAS. The results also meet the EPA SW-846 expected ranges of accuracy and reproducibility.

4.12.1 Recovery Studies on Standard Solution Performed by ICP/MS

4.5 ppb standard Cd solution, 7.75 ppb Cr standard solution, and 10.4 ppb Pb standard solutions were analyzed by ICP-MS. Cd and Pb standard solution were sorbed on 0.25g Chelex 100. Cr standard solutions were preconcentrated on 0.25 g Dowex 1x8. The relative standard deviation and accuracy are shown on Table 15. The results are comparable to the results from the EPA method, and are presented in Table 4.18.

Table 4.18 Recovery study on standard solution by ICP/MS

	1	2	3	4	Mean	SD	%RSD	% Effic.
Cd	4.41	4.62	4.08	4.55	4.42	0.24	5.43	98.22
Cr	8.09	6.05	8.29	7.56	7.50	1.01	13.51	96.77
Pb	8.44	10.18	10.79	11.27	10.17	1.24	12.19	97.79

The relative standard deviation (RSD) and efficiencies are calculated as follows:

%RSD = (SD/Mean) x 100

%Efficiency = (Mean value/Expected value) x 100

4.12.2 Recovery Study Performed on ICP/MS Analyses from EPA SW-846

Recovery study on Cd, Cr, Pb of aqueous samples performed on ICP/MS was done by USEPA. The relative standard deviation and comparability range are presented in Table 4.19.

Table 4.19 EPA SW-846 Module Method #: 6020 (for aqueous samples)

	%RSD range	Comparability range
Cd	4.6 - 7.2	98 - 102
Cr	13 - 27	95 - 105
Pb	11 - 23	71 - 137

Comparability: Percentage agreement of mean ICP-MS values to those of the reference technique.

4.12.3 Recovery Study on Parsippany Lake Water by ICP/MS

Parsippany Lake water (Parsippany, NJ) was analyzed using Chelex-100 (for Cd, Pb) and Dowex 1x8 (for Cr(VI)) preconcentration procedure. The lake water samples were then spiked with 0.08 ppb Cd, 0.2 ppb Pb, and 0.2 ppb Cr standard solution. The results are presented in Table 4.20.

Table 4.20 Spike 0.08 ppb Cd, 0.2 ppb Cr(VI), and 0.2 ppb Pb on Parsippany Lake water by ICP/MS analysis

	1	2	3	Mean	SD	%RSD
Cd, Lake water	0.0231	0.0221	0.0244	0.0232	0.0012	5.17
Lake water +spike	0.1001	0.1015	0.1047	0.1021	0.0024	2.35
Cr(VI), Lake water	0.1500	0.1670	0.1870	0.1680	0.0185	11.02
Lake water +spike	0.3356	0.3601	0.3861	0.3606	0.0253	7.02
Pb,Lake water	0.2012	0.2058	0.2347	0.2139	0.0182	8.51
Lake water +spike	0.3725	0.4056	0.4459	0.4080	0.0368	9.02

The spike recoveries for Cd, Cr, and Pb are as follows:

%Recovery for Cd = 100(0.1021-0.0232)/0.08 = 98.63

%Recovery for Cr = 100(0.3606-0.1680)/0.2 = 96.30

%Recovery for Pb = 100(0.4080-0.2139)/0.2 = 97.05

4.12.4 Determination of Cd, Cr, and Pb in Drinking Water and Parsippany Lake Water (April 1997) by ICP/MS

EPA method and ion exchange resin method were used for sample preparation. The results are presented in Table 4.21 for drinking water and Parsippany Lake water.

Table 4.21 Average total and average exchangeable metals in drinking water and Parsippany Lake water, Unit: ppb

(1) Drinking Water Element	Avg. Total (EPA Method)	Avg. Exchangeable (Developed Method)
Cd	0.025	0.023
Pb	1.68	1.450
Cr(VI)	0.060*	0.057

(2) Parsippany Lake Water Element	Avg. Total (EPA)	Avg. Dissolved (EPA)	Avg. Exchangeable (Developed Method)
Cd	0.031	0.023	0.022
Pb	0.880	0.280	0.275
Cr(III)			0.046
Cr(VI)			0.110
Total Cr	0.240*	0.160*	

Note: * EPA method does not distinguish between Cr(III) and Cr(VI), but measures both.

There are some differences between average total metals by EPA method and average ion exchange method with Chelex-100 (Cd, Pb) or Dowex 1x8 (Cr(VI)) preconcentration procedures. These differences can be attributed to the strongly chelated metals or metals bound to colloidal or particulate matter that inhibit the absorption of the metal on the ion exchange resin.

The data show nearly identical values for the average dissolved metals by the EPA method and the average ion exchange metals. It is clear that almost all the dissolved metals are exchangeable.

4.13 Seawater Sample

A seawater sample was collected at Sandy Hook, NJ. The pH of the seawater is 7.46. The seawater sample was stirred with Chelex 100 resin to sorb Cd, Pb, and Cr(III). The sample was also stirred with Dowex1x8 for Cr(VI). The metal-loaded resins were then washed off with 5 ml 5% nitric acid into a test tube.

Table 4.22 Study of fortified seawater samples

	mean	%RSD(n=3)	% recovery of spike
Cd, seawater	0.025	10	
spike 0.02 ppb Cd	0.043	4.6	90
Pb, seawater	0.286	3.9	
spike 0.4 ppb Pb	0.69	3.3	95.5
Cr(VI),seawater	0.141	4.3	
spike 0.2 ppb Cr(VI)	0.308	4.2	83.5

A spike study was also done on the seawater (Figure 4.11). Although the recoveries are not as high as those from fresh water, Chelex 100 resin was found to be useful in a seawater sample. Since sulfate and other anions compete with the sorption of trace amounts of Cr(VI), sorption on Dowex was not as efficient in this high salt matrix (Table 4.22).

4.14 Conclusions on Water Samples

An analytical method for the trace metals which are preconcentrated by adsorption on ion exchange resin and then determination of these metals, (Cd, Pb, Cr(III), Cr(VI)) in natural waters and the analysis of the metals by GFAAS and/or ICP-MS has been developed. The natural waters here include river water, lake water, seawater, and drinking water. The distribution of the metals in particulate matter, complexed or colloidally bound metals, and free ions was determined.

The current EPA method for the determination of total dissolved metals includes complexed and colloidal forms. The developed method was focused on the free ions. Both the EPA method and the developed method were used in this study for obtaining information on the fraction of the metals present in bound and free forms.

Ion exchange resin may be used in either a column or a batch method. The column method involves passing the sample through a column, filled with the ion exchange resin to achieve the separation. The metals are removed from the column by elution with a reagent solution. The most effective agents to elute the metals from the ion exchange resin are

acids. The batch method which involves the addition of resin directly into the sample followed by stirring is the method used in this study. The batch method requires less reagent, and contamination can be minimized.

In contrast to sorption in a column, sorption on ion exchange resin stirred with the water samples provide a homogeneous distribution of the metals on the resin. This allows direct analysis of the resin as a slurry using GFAAS.

Less handling of water samples, easier transportation and better preservation of the samples results from the use of a batch ion exchange method. The GFAAS temperature program is optimized with the pyrolysis temperature at 490 °C for Pb, 250 °C for Cd, and 800 °C for Cr analysis. The maximum metal absorption will be produced and the background interference will be minimized using these programs.Experiment shows identical results without added Pd matrix modifier by using the optimized temperature program. Pd matrix modifier is not necessary when using these programs.

The water sample has to be buffered at pH5 using an acetate buffer to achieve the optimized adsorption efficiency in the Chelex 100 preconcentration process. It is not necessary use a buffer solution in the Dowex1x8 preconcentration process.

The method detection limit of the resin preconcentration process with GFAAS and ICP/MS is 0.0075 ppb for Cd, 0.04 ppb for Pb, and 0.05 ppb for Cr(VI). It is possible to reduce the method detection limit further by increasing the concentration ratio. This can be achieved by increasing the water volume, and concentrating to a smaller volume by using less acid to desorb the metals from the resin.

In tap water, river water, and lake water, little difference was found between dissolved metals and exchangeable metals. This indicates that in the tested samples 90% of the dissolved metal content is exchangeable.

Although ICP-MS is more costly than Flame AA or GFAA, it is a true multielement analytical technique with excellent sample throughput. It also has very good sensitivity. ICP-MS is favored where large numbers of samples are going to be analyzed. In comparison to Flame AA or GFAA, the analysis time for multielement by ICP-MS is much reduced.

The major advantages of the developed method can be summarized as follows:

* Preconcentration: Metals in natural water are normally at sub ppb level and are not easily analyzed even with a modern instrument such as GFAAS. Evaporation is commonly used for the preconcentration. Since evaporation is a lengthy process, it has substantial possibility for the contamination of the sample. The ion exchange resin method offers an additional advantage of a relatively short time period for sample preparation and minimal effort.
* Speciation: The species of metals which are most mobile, and most bioavailable in the environment are those most readily sorbed by the ion exchange resins. The ion exchange method therefore gives results which may be more ecologically meaningful.
* Convenient storage and transport: When the metals present in the water sample are preconcentrated on 0.25 g of resin, the samples are very light weight, and easy to carry and store, compared with the heavy water samples. They are also stable in storage and interconversion of Cr (III) and Cr (VI) is eliminated.

CHAPTER 5

SPECIATION OF TRACE ELEMENTS IN SEDIMENT USING SEQUENTIAL SELECTIVE EXTRACTANTS AND GFAAS

5. 1 Experimental

5.1.1 Equipment

In addition to equipment used for speciation and determination of trace metals in water samples, the following equipment, procedures, and reagents were used.

The microwave digestion system model MDS 2100, was supplied by CEM Inc. Its maximum power output is 1000 W. An maximum temperature of 175 °C, maximum pressure of 175 psi, and 100% power was used for sample digestion. Advanced composite vessels were used inside the microwave oven for sample preparation. The vessels consist of a liner and cover to contain a sample solution. The material of the vessels is transparent to microwave energy. The sample solution inside the liner absorbs the microwave energy. The volume of vessel is 100 ml, and its maximum operating temperature and pressure is 200 ° C and 200 psig. The body, cover, vent fitting, ferrule nut, rupture membrane, sleeve, and vent tubing of the vessel were made from Teflon PFA, a registered trademark of the E.I. DuPont Company. The thread ring and cap were made of Ultem, a registered trademark of the General Electric Company. CEM also recommended that concentrated base or salt solutions, certain mineral and organic solvents such as alkanes, ketones, ethers, are unsuitable for use in these advanced composite vessels.

Cleaning of microwave vessels was performed after each operation according to manufacturer's recommendation.

The centrifuge used was supplied by IEC, Model HN-SII. Its maximum speed is 9000 rpm.

5.2 GFAAS Operating Conditions and Optimized Furnace Program

Both operating conditions and furnace programs for Cr, Pb are the same as described in Chapter 4 for water sample analysis (section 4.1.2). The operating conditions are also the same for Cd. However, the furnace program is slightly modified, for each extractant solution used (Table 5.1).

5.3 Reagents

In addition to reagents used for water analysis, the following reagents were also used for sediment characterization:

- Glacial Acetic Acid (CH_3COOH): 99+%, Sigma Chemical Company
- Ammonium acetate (NH_4OAc, or , CH_3COONH_4):from Fluka, Inc.
- Hydroxylamine hydrochloride ($NH_2OH.HCl$): Amend Drug & Chemical Co.
- Sodium acetate: analytical reagent, Mallinckrodt Chemical Works, St. Louis, MO 63160
- Hydrogen Peroxide 30%: Reagent grade. (Fisher Chemical, Fisher Scientific)

Table 5.1 The Optimized Furnace Program for Cd

	Drying	Pyrolysis I	Pyrolysis II	Atomization	Cleaning
Temp.(°C)	See below: (1), (2), (3), (4), (5)				2200
Ramp(°C/sec)	2	10	10	0	
Hold(sec)	0	0	0	4	3
Purge	1	2	1	0	3

(1) For Cation exchanging extractant: 1M NH_4OAc

Dry	Py I	Py II	Atom	Clean
150	200	490	1700	2200

(2) For Carbonate extractant: 1M HOAc-NaOAc pH = 5.15

Dry	Py I	Py II	Atom	Clean
150	200	700	1800	2200

(3) For Acidic, reducing extractant: 1M $NH_2OH.HCl$, buffer with 0.1M HNO_3 to pH < 3

Dry	Py I	Py II	Atom	Clean
150	200	600	1700	2200

(4) For Oxidizing extractant: release organic bound metals: 30% H_2O_2

Dry	Py I	Py II	Atom	Clean
150	200	600	1700	2200

(5) For Residual Mineral Extractant: Conc. HNO_3

Dry	Py I	PyII	Atom	Clean
150	200	490	1700	2200

5.4 Speciation and Analytical Determination of Cd, Cr, and Pb in New Jersey Marine Sediments

5.4.1 Sediment Samples

Sediments under the thick layer of natural water were transported in plastic jars to the laboratory within three hours. Speciation and determination of the target metals using both regular and microwave digestion procedures were started the same day. The same five step extraction and the same reagents were used for both procedures. Reagents used and time of extraction are presented in Table 5.2. Regular and microwave extractions were performed in parallel, with the same samples. EPA method [64] for determination of total metals content in sediments using microwave digestion was also performed and the results were compared.

The sediment samples were collected from (1) South Shore of Shark River estuary, NJ (Sep. 08, 1997) (2) Newark Bay, NJ (June 1997) (3) Atlantic City Bay, NJ (June 1997).

About 20 grams of each sample were dried overnight at 35 °C, passed through a 40 mesh sieve, then homogenized in a blender for 1 minute. Replicates of the homogenized sample were taken for analysis.

5.5 Experimental Procedure for Sediment Speciation

Total metal concentrations were determined by the standard EPA procedure [64]. Speciation of sediment samples for Cd, Cr,and Pb were carried out using two different sequential extraction procedures: the modified Tessier method (MTM)[67] and microwave (MWM) assisted sequential extraction. For both methods, a 5 step extraction

procedure with the same reagents was used. Reagents and and extraction times are presented in Table 5.2.

After trial experiments using a single extraction procedure, kinetics of the sequential extraction using MTM and MWM was investigated.

Because the application of microwave sequential extraction for sediment speciation is relatively new, preliminary experiments were performed for MWM. The results of these studies are presented in the next chapter.

Attempts were also made to spike natural sediments with metals in specific forms (for example: lead for carbonate bound fraction).

The extraction efficiency is a function of the extraction time, the extractant nature, the ratio of the amount of sample to the volume of extractant, and the temperature and pressure of the extraction process in MWM. Effects of the listed parameters on extraction efficiency were investigated.

After optimization of extraction procedures, natural sediment samples were analyzed for the metals of interest. Reproducibility and accuracy of investigated sequential extraction procedures were evaluated.

There are 5 steps used in the published Tessier sequential extraction procedure [3]. These five steps involve extraction of the sediment by stirring of the sediment and extractant. Only the 4th step, using 30% hydrogen peroxide, involves heating as well as stirring. The modified Tessier method was used in this work [67].

The same 5 step sequential extractants were used, for much shorter times using the microwave technique. The sediments were digested with each extractant for a short period

of time in the microwave electromagnetic field. Both the MTM and MWM sequential extraction methods were compared with the EPA procedure [64] for total metals in soil and sediment using microwave digestion.

The five step microwave sequential extraction procedure used in this experiment is as follows:

First step, to extract readily exchangeable metals: Seal 0.2 g of sample with 10 ml 1 M NH_4OAc into a microwave vessel. Shake it well and then heat it for 90 second with 100% microwave power. Pour the solution and sediment into a clean test tube, centrifuge it, and pour the clear solution into another clean plastic test tube(Label A). Keep the sediment in the first test tube.

Second step, to extract specifically sorbed, carbonate bound metals: Add 10 ml of 1M NaOAc-HOAc into the test tube containing the sediment from step 1. Pour the mixture into a clean microwave vessel. Shake it well and heat it for 90 second at 100% power. Centrifuge it and then pour the clear solution into a clean plastic test tube (Label B). Keep the sediment in the second test tube.

Third step, to extract metals from easily reducible substrates and release the metals associated with iron(III) or manganese(IV) oxide: Add 10 ml 1M $NH_2OH.HCl$ buffered with 0.1 M HNO_3, into the tube containing the sediment from step 2 and mix it. Pour the mixture into the microwave vessel. Shake it well and heat it for 90 second with 100% power. Centrifuge it and then pour the clear solution into a new plastic test tube (Label C). Keep the sediment in the third test tube.

Forth step, extraction from oxidizable materials to release organic bound metals: Add 10 ml 30% H_2O_2 into the test tube containing sediment from step 3. Mix it well and pour into a microwave vessel. Shake it well and heat for 180 second with 100% power, then cool it, centrifuge it and pour the clear solution into a clean plastic test tube (Label D). Keep the sediment in the test tube.

Fifth step, for metals in residual minerals: Add 10 ml concentrated nitric acid into the test tube containing sediment from step 4. Mix it well and then pour the mixture into a microwave vessel. Shake it well and heat for 3 min. with 100% power, cool it, centrifuge it and keep the sediment in the test tube (Label E).

Each sediment sample was mixed with the extractant and predigested at room temperature in a hood for a minimum of 10 minutes before using microwave. The microwave method developed here was based on processing 2 vessels at a time. If more vessels are used, a longer time is needed to reach the same temperature and pressure in the sample vessels.

Extraction time is dramatically reduced in each step by this microwave enhanced extraction technique compared with the Modified Tessier Method (Table 5.2).

After each extraction step, samples were centrifuged for 2 minutes at 3000 rpm. The liquid phase was decanted and used for GFAAS analysis.

5.6 Results and Discussions

5.6.1 Microwave Digestion with Different Extractants

Prior to speciation and determination of trace elements in sediments, preliminary experiments were carried out in order to determine kinetics of sequential extraction, and the precision and accuracy of the measurements.

Table 5.2 Time of sequential extraction of sediments using MTM and MWM

		MTM	MWM
Step & Target species	Reagent	Time	Time
1. Exchangeable Metals	1M NH_4Oac	24 hours	90 second
2. Carbonate bound Metals	1M NaOAc-HOAc	5 hours	90 second
3. Metals bound to Fe/Mn-oxide	1M $NH_2OH.HCl$ + 0.1M HNO_3	30 minutes	90 second
4. Organic bound Metals	30% H_2O_2	2 hours	3 minutes
5. Metals in residual	Concentrated HNO_3	30 minutes	4 minutes

5.6.1.1 Temperature and Pressure of Microwave Procedure: Measurements of temperature and pressure during microwave digestion are necessary because microwave apparatus differs in power and conditions must be the same if data are to be compared. Atlantic City Bay sediments were used for these experiments.

The microwave digestion temperature and pressure program was preset at maximum 175 °C and 175 psi. The microwave power output was 100%, the fan speed was 100%. The maximum power was 1000 W.

In order to understand the effect of temperature and pressure on extraction, temperature and pressure of 0.15 g sediment samples were measured during 3 minutes of microwave digestion. This process was carried out for all five extractants. Some observations are presented below:

1) 10 ml 1M NH_4OAc + 0.15g sediment: The temperature and pressure of the sample increased with time. The temperature reached 175 °C and pressure reached 150 psi within 90 second.
2) 10 ml 1M NaOAc-HOAc pH 5.17 + 0.15 g sediment: The temperature reached 190 ° C within a 45 second extraction time, and reached 175 psi within 40 second. Because maximum temperature and maximum pressure were preset at 175 ° C and 175 psi, microwave power is stopped when the set points are exceeded. Therefore, the temperature and pressure will go down once the maximum is reached and oscillate as power is turn on and off.
3) 10 ml 1M $NH_2OH.HCl$ buffered with 0.1 M HNO_3 + 0.15 g sediment: The temperature reached 180 ° C at 75 second, and the pressure reached 175 psi at 70 second. After reaching this point, temperature and pressure oscillated within a range of 10 ° C and 100 psi. The temperature ranged between 170 and 180 °C, and the pressure between 175 and 75 psi.
4) 10 ml 30% H_2O_2 + 0.15 g sediment: The temperature reached 180 °C at 45 second, and the pressure reached 190 psi at 35 sec, and then the temperature ranged between 175 and 183 °C, the pressure between 150 and 185 psi.

5) 10 ml Conc. HNO_3 + 0.15 g sediment: The temperature and pressure reached the maximum point 180 °C and 110 psi at 70 second. After this point, the temperature ranged between 170 and 175 °C, and the pressure range between 50 and 100 psi.

5.6.2 Effect of NH_4OAc Concentration on Microwave Assisted Digestion

Because the exchangeable fraction of sediments is of particular interest, different concentrations of ammonium acetate were evaluated for extraction of this fraction. Time of digestion was 90 second.

1 M NH_4OAc and 4.5 M NH_4OAc were used for extraction of the exchangeable metals from sediment. It was found that for Cr and especially for Pb, higher concentration of the extractant significantly increased extraction efficiency. Results of extraction with 1M NH_4OAc are more consistent on sediments from different sites (Figure 5.1). 1 M NH_4OAc was selected for extraction of exchangeable metals in further experiments. This reagent is also commonly used in Tessier extraction procedures [3]. Results of extraction of Cd, Cr, and Pb from different sediments with 1M NH_4OAc and 4.5M NH_4OAc are presented in Table 5.3.

5.6.3 Kinetics of Sequential Extraction Procedure

Kinetics of sequential extraction using Modified Tessier Method (MTM) and Microwave Method (MWM) were investigated. Reagents for the 5 step extraction are listed in Table 5.2. The goal of these experiments was to select extraction time for speciation of real

samples. Sediments from Atlantic City Bay were used for this study. Sediments were also analyzed for total metal content by the EPA method. Total average concentrations of 1.24 ppm(w/w) Cd, 60.2 ppm (w/w) Cr, and 37.24 ppm (w/w) Pb were found in the sediment sample.

Table 5.3 Cd, Cr, and Pb fractions digested for 90 second from sediments with 1M and 4.5 M NH_4OAc

Sediment		1M NH4Oac	4.5M NH4Oac
		% of Total metal	% of Total metal
Shark River:	Cd	49.32	63.51
	Cr	2.55	17.14
	Pb	2.95	43.70
Newark Bay:	Cd	47.41	44.83
	Cr	2.19	6.89
	Pb	23.35	51.41
Atlantic City Bay:	Cd	41.13	36.89
	Cr	2.39	1.56
	Pb	5.51	20.76

5.6.3.1 Modified Tessier Method (MTM): Kinetics studies on spiked and nonspiked sample using 5 step sequential extraction technique were carried out. In order to

understand the behavior of each metal fraction, four different time periods were used for this study. Results from Modified Tessier Method for Cd, Cr, and Pb are presented in Table 5.4 and Figure 5.2-5.6.

As a result of kinetics studies of sequential extraction using MTM, the following extraction times were selected for speciation of trace metals in sediments.

Step 1: exchangeable metals, 24 hours

Step 2: Carbonate bound metals, 5 hours

Step 3: Metals bound to Fe/Mn-oxide, 30 minutes

Step 4: Metals in organic matter, 2 hours

Step 5: Metals in residual, 30 minutes

It is supposed that the further increase of regular extraction time does not significantly affect metals distribution between fractions. Sum of 5 step extraction is close to total metal concentration in sediment found by the standard EPA method.

5.6.3.2 Microwave Method (MWM): Kinetics studies of sequential extraction using microwave has been also performed. The same steps and reagents were applied for identical the metals in sediment samples.

Four different time periods were used for this study. Results from MWM for Pb, Cr, and Cd are presented in Table 5.5 and Figure 5.7-5.11.

Table 5.4 Kinetics of Sequential Extraction using Modified Tessier Method (MTM), unit: ppm (w/w)

Step	1. Exchan-geable	2. Carbon-ate	3. Fe/Mn-oxide	4. Organic matter	5. Residual	Sum 1-5	EPA Total
K1, Extract Time	**0.5 hour**	**1 hour**	**15 mins.**	**30 mins.**	**15 mins.**		
Pb	0.64	7.86	18.55	4.07	1.15	32.27	37.24
Cr	0.46	1.35	4.03	28.53	14.62	48.99	60.20
Cd	0.43	0.04	0.39	0.08	0.03	0.97	1.24
K 2, Extract Time	**1 hour**	**3 hour**	**0.5 hour**	**1 hour**	**0.5 hr**		
Pb	0.64	8.70	18.75	4.20	1.28	33.57	37.24
Cr	0.63	2.37	5.60	29.54	13.12	51.26	60.20
Cd	0.43	0.04	0.45	0.08	0.02	1.02	1.24
K 3, Extract Time	**12 hour**	**5 hour**	**1 hour**	**2 hour**	**1 hour**		
Pb	0.65	9.80	18.95	4.40	1.39	35.19	37.24
Cr	0.70	2.80	6.00	30.50	13.65	53.65	60.20
Cd	0.53	0.04	0.45	0.08	0.04	1.14	1.24
K 4, Extract Time	**24 hour**	**8 hour**	**2 hour**	**4 hour**	**2 hour**		
Pb	0.67	9.85	19.12	4.58	1.49	35.71	37.24
Cr	0.89	2.88	8.04	32.70	10.46	54.97	60.20
Cd	0.58	0.05	0.45	0.07	0.05	1.20	1.24

Table 5.5 Kinetics of sequential extraction using microwave method (MWM), Unit: ppm (w/w)

Step	1. Exchan-geable	2. Carbon-ate	3. Fe/Mn-oxide	4. Organic matter	5. Residual	Sum 1-5	EPA Total
K1, Extract Time	**20 sec**	**20 sec**	**20 sec**	**20 sec.**	**20 sec.**		
Pb	1.43	6.38	17.35	2.62	1.27	29.05	37.24
Cr	1.09	1.72	11.65	18.03	6.68	39.17	60.20
Cd	0.35	0.04	0.40	0.05	0.03	0.89	1.24
K2, Extract Time	**50 sec.**	**50 sec.**	**50 sec.**	**50 sec.**	**50 sec.**		
Pb	2.09	6.00	20.72	2.57	0.91	32.29	37.24
Cr	1.37	1.70	24.36	14.59	8.68	50.70	60.20
Cd	0.51	0.04	0.60	0.05	0.03	1.23	1.24
K3, Extract Time	**90 sec.**	**90 sec.**	**90 sec.**	**90 sec.**	**90 sec.**		
Pb	2.40	3.13	23.70	2.82	1.23	33.28	37.24
Cr	1.57	0.55	25.72	11.55	13.30	52.69	60.20
Cd	0.51	0.04	0.60	0.05	0.03	1.23	1.24
K4, Extract Time	**180 sec.**	**180 sec.**	**180 sec.**	**180 sec.**	**180 sec.**		
Pb	2.42	3.15	26.93	2.87	1.46	36.83	37.24
Cr	9.35	0.43	30.49	8.05	11.41	59.73	60.20
Cd	0.51	0.04	0.60	0.05	0.04	1.24	1.24

It is clear that results of microwave extraction are change rapidly with time. Results for Cd are more stable, while concentrations of Pb and Cr in different fractions change significantly. For example, concentration of Pb and Cr increase with time in

fraction one and decrease in fraction two, indicating that some carbonate bound metals are digested during the first step, when longer times are used.

Longer periods of microwave sequential extraction at lower percent of the oven power (25-50%) are recommended in the literature [80]. To our knowledge, the referred article is the only publication about microwave assisted sequential extraction of sediments. It was published after completion of our experiments. In our opinion, it may be beneficial to increase extraction time and reduce power of the oven to avoid excessive evaporation of the sample. However, periods of time 20-30 minutes used for microwave extraction steps in [80] look excessive.

From our data, a microwave extraction time of 90 second was selected for sequential extraction of exchangeable metals, carbonate bound metals, and metals bound to Fe/Mn-oxide. Three minutes was used for extraction of organic bound metals, and four minutes for the extraction of metals in the residual fraction. The sum of concentrations in the five fractions obtained from 90 second sequential extraction using MWM is also close to the total metal concentrations measured by the EPA method.

It can be concluded that analytical data obtained using MTM and MWM are correlated. Distribution results for Cd are very similar for all fractions. For Cr and Pb, results are typically higher for exchangeable fraction when MWM was used. At the same time they are higher for carbonate bound fraction when MTM was applied. Apparently some carbonate bound fraction may be digested in the step one when microwave energy is used.

5.6.3.3 Spike Study for Sediments: Two materials were prepared to use as spike substances for the sediment: a solid carbonate contaminated with Pb, and peat moss with Pb sorbed on it. Each of these was added into the sediment sample before extraction. The five step sequential extraction was used.Analyses of these spiked samples were performed to attempt to determine the efficiency of the 2nd step for metals bound to carbonate, and the 4th step for metals bound to organic matter. The materials prepared for spiking were characterized by being digested with concentrated nitric acid, using the EPA microwave technique and then analyzed using GFAAS for determination of total concentration of Pb. 0.024% Pb was found in the prepared contaminated $CaCO_3$. The peat moss itself was found to contain 0.02735% Pb.

5.6.3.3.1 The Procedure for the Preparation of Spike Sample: An attempt was made to prepare synthetic materials to test the extraction of the various classes of bound metals. Calcium carbonate was precipitated from a lead-containing solution to make a lead-contaminated carbonate, and peat moss, which had a measurable lead contamination itself. These were used to spike sediment samples to determine in which fraction the added metals were extracted. The experiment was only partially successful, as much of the synthetically added metals were extracted in the initial step, indicating that they were not bound into the matrix as thoroughly as in natural soils or sediments.

** Preparation of Pb-contaminated carbonate

5.5 g $CaCl_2$ + 90 ml H_2O + 20 ml solution of Na_2CO_3 with $Pb(NO_3)_2$ added ---> stir

2 hours and then overnight settling --> collect on filter paper

5.6.3.3.2 Definition of Recovery by EPA: EPA defines the recovery as follows:

$$\% \text{ Recovery} = 100 (X_s - X_u) / K$$

Where:

X_s: measured concentration for the spiked sample

K: known concentration of the spike in the sample

X_u: Measured concentration of the unspiked sample

Originally, were 1.24 ppm(w/w) Cd, 60.2 ppm (w/w) Cr, and 37.24 ppm (w/w) Pb in the sediment sample from Atlantic City Bay. The spiking materials were then added into sediment sample. The efficiency of the recovery was determined at different extraction times. The recovery was based on the sum of each fraction, then compared with the total concentration of the unspiked sediment samples. The efficiency of the extraction procedure was calculated by comparing the total metal concentration from specific procedure to the expected total metal concentration from EPA microwave method.

5.6.3.3.3 Studies of the Spiked Sediment Using MTM: MTM was carried out using several different times extractions to determine the extraction rates for the spiked materials.

1) MTM schedule 1 was the sequential extraction procedure with the shortest extraction time used at each step.

Enough lead-contaminated carbonate was added to the sediment to increase the Pb concentration by 2 ppm. Contaminated peat moss was added to increase the Pb concentration by 19.6 ppm. Good agreement was found in the second step, but most of

the organic bound lead appeared to be extracted in the first step. This may indicate that a material such as peat moss has ion exchange sites as well as stronger binding sites. The total recovery on Pb is 72.08% with schedule 1 (Table 5.6).

Table 5.6 Kinetic and recovery study by MTM, Schedule 1, unit: ppm (w/w)

Pb	1.Excha-ngeable	2.Carbon-ate	3. Fe/Mn-oxide	4.Organic Matter	5. Residual	Sum1-5
MTM time	0.5 Hr	1 Hr	15 min	30 min	15 min	
Sediment	0.64	7.86	18.55	4.07	1.15	32.27
Actual	0.64	9.93	18.55	23.71	1.15	55.48
Experi-mental	1.69	9.98	28.72	7.08	1.53	49.00

Spike Pb-contaminated carbonate = 2.07 PPM (for step 2)

Spike organic-Pb = 19.64 PPM (for step 4)

Total Spike = 23.21 PPM

Recovery = (49.0-32.27)/23.21x100% = 72.08%

Efficiency = real/expected = 32.27/37.24 x100% = 86.65%

2) The extraction time used on stir schedule 2 is a little longer than schedule 1. The efficiency of extraction of total metals with schedule 2 was 90.15% for Pb. Good agreement was found in the second step, but most of the organic bound lead appeared to be extracted in the third step. The total spike Pb is 19.66 ppm. The total recovery on Pb is 88.61% with schedule 2 (Table 5.7).

Table 5.7 Kinetic and recovery study by MTM, Schedule 2, Unit: ppm (w/w)

Pb	1.Excha-ngeable	2.Carbon-ate	3. Fe/Mn-oxide	4.Organic Matter	5. Residual	Sum1-5
MTM time	2 Hr	3 Hr	30 min	1 Hr	30 min	
Sediment	0.64	8.70	18.75	4.20	1.28	33.57
Actual	0.64	11.27	18.75	20.39	1.28	53.23
Experi-mental	1.26	11.36	30.83	6.24	1.30	50.99

Spike lead-contaminated carbonate = 2.57 PPM (for step 2)

Spike organic-Pb = 16.19 PPM (for step 4)

Total Spike = 19.66 PPM

Recovery = (50.99-33.57)/19.66x100% = 88.61%

Efficiency = 33.57/37.24 x 100% = 90.15%

3) The extraction time used on stir schedule 3 is a little longer than stir schedule 2. The efficiency of extraction of total metals with schedule 3 was 94.50% for Pb, 89.12% for Cr, 91.94% for Cd. Good agreement was found in the second step, but most of the organic bound lead appeared to be extracted in the third step. The total recovery on Pb is 92.97% with schedule 3 (Table 5.8).

Table 5.8 Kinetic and recovery study by MTM, Schedule 3, Unit; ppm (w/w)

Pb	1.Excha-ngeable	2.Carbon-ate	3. Fe/Mn-oxide	4.Organic Matter	5. Residual	Sum1-5
MTM time	12 Hr	5 Hr	1 Hr	2 Hr	1 Hr	
Sediment	0.65	9.80	18.95	4.40	1.39	35.19
Actual	0.65	13.12	18.95	20.28	1.39	51.07
Experi-mental	1.81	13.44	30.27	5.73	1.79	53.04

Spike Pb-contaminated carbonate = 3.32 PPM (for step 2)

Spike organic-Pb = 15.88 PPM (for step 4)

Total Spike = 19.2 PPM

Recovery = (53.04-35.19)/19.2x100% = 92.97%

Efficiency = 35.19/37.24 x 100% = 94.50%

4) The extraction time used on stir schedule 4 is a little longer than stir schedule 3. The efficiency of extraction of total metals with schedule 4 was 95.89% for Pb (Table 5.9 and Figure 5.12).

5.6.3.3.4 Studies of the Spiked Sediment Using MWM: 1) Microwave schedule 1 was the sequential extraction procedure with an extraction time of 20 second used at each step. The efficiency of extraction of total metals with microwave schedule 1 was 78.01% for Pb. 71% agreement was found in the second step, and most of the organic bound lead appeared to be extracted in the third step. The total recovery on Pb is 73.33% with microwave schedule 1 (Table 5.10).

Table 5.9 Kinetic and recovery study by MTM, Schedule 4, Unit: ppm (w/w)

Pb	1.Excha-ngeable	2.Carbon-ate	3. Fe/Mn-oxide	4.Organic Matter	5. Residual	Sum1-5
MTM time	24 Hr	8 Hr	2 Hr	4 Hr	2 Hr	
Sediment	0.67	9.85	19.12	4.58	1.49	35.71
Actual	0.67	13.01	19.12	23.07	1.49	57.36
Experi-mental	2.12	14.09	32.83	5.39	1.92	56.35

Spike Pb-contaminated carbonate = 3.16 PPM (for step 2)

Spike Peat Moss (Pb) = 18.49 PPM (for step 4)

Total Spike = 21.65 PPM

Recovery = (56.35-35.71)/21.65x100% = 95.00%

Efficiency = 35.71/37.24 x 100% = 95.89%

Table 5.10 Kinetic and recovery study by MWM, Schedule 1, Unit: ppm (w/w)

Pb	1.Excha-ngeable	2.Carbon-ate	3. Fe/Mn-oxide	4.Organic Matter	5. Residual	Sum1-5
MW time	20 sec	20 sec	20 sec	20 sec	20 sec	
Sediment	1.43	6.38	17.35	2.62	1.27	29.05
Actual	1.43	9.72	17.35	23.35	1.27	53.12
Experi-mental	2.19	8.73	31.08	3.20	1.50	46.70

Spike Pb-contaminate carbonate = 3.34 PPM (for step 2)

Spike Peat Moss (Pb) = 20.73 PPM (for step 4)

Total Spike = 24.07 PPM

Recovery = (46.70-29.05)/24.07x100% = 73.33%

Efficiency = 29.05/37.24 x 100% = 78.01%

1) Microwave schedule 2 use an extraction time of 50 second at each step. The efficiency of extraction of total metals with microwave schedule 2 was 86.71% for Pb. Good agreement was found in the second step, but most of the organic bound lead appeared to be extracted in the third step. The total recovery on Pb is 83.47% with schedule 2 (Table 5.11).

Table 5.11 Kinetic and recovery study by MWM, Schedule 2
Unit: ppm(w/w)

Pb	1.Excha-ngeable	2.Carbon-ate	3. Fe/Mn-oxide	4.Organic Matter	5. Residual	Sum1-5
MW time	50 sec	50 sec	50 sec	50 sec	50 sec	
Sediment	2.09	6.00	20.72	2.57	0.91	32.29
Actual	2.09	9.54	20.72	21.41	0.91	54.67
Experi-mental	2.50	9.21	34.98	3.17	1.11	50.97

Spike Pb-contaminated carbonate = 3.54 PPM (for step 2)

Spike Peat Moss Pb) = 18.84 PPM (for step 4)

Total Spike = 22.38 PPM

Recovery = (50.97-32.29)/22.38x100% = 83.47%

Efficiency = 32.29/37.24 x 100% = 86.71%

3) Microwave schedule 3 used an extraction time of 90 second at each step. The efficiency of extraction of total metals with microwave schedule 3 was 89.37% for Pb. 85% agreement was found in the second step, but most of the organic bound lead appeared to be extracted in the third step. The total recovery on Pb is 91.07% with schedule 3 (Table 5.12).

Table 5.12 Kinetic study by MWM, Schedule 3, Unit: ppm (w/w)

Pb	1.Excha-ngeable	2.Carbon-ate	3. Fe/Mn-oxide	4.Organic Matter	5. Residual	Sum1-5
MW time	90 sec	90 sec	90 sec	90 sec	90 sec	
Sediment	2.40	3.13	23.70	2.82	1.23	33.28
Actual	2.40	7.39	23.70	19.73	1.23	54.45
Experi-mental	2.99	6.75	37.29	3.97	1.56	52.56

Spike Pb-contaminated carbonate = 4.26 PPM (for step 2)

Spike Peat Moss (Pb) = 16.91 PPM (for step 4)

Total Spike = 21.17 PPM

Recovery = (52.56-33.28)/21.17x100% = 91.07%

Efficiency = 33.28/37.24 x 100% = 89.37%

4) Microwave schedule 4 used an extraction time of 180 second at each step (Figure 5.13). The efficiency of extraction of total metals with microwave schedule 4 was 98.90% for Pb. Good agreement was found in the second step, but most of the organic bound lead appeared to be extracted in the third step. The total recovery on Pb is 98.03% with microwave schedule 4 (Table 5.13).

Table 5.13 Kinetic and recovery study by MWM, Schedule 4, Unit: ppm (w/w)

Pb	1.Excha-ngeable	2.Carbon-ate	3. Fe/Mn-oxide	4.Organic Matter	5. Residual	Sum1-5
MW time	180 sec	180 sec	180 sec	180 sec	180 sec	
Sediment	2.42	3.15	26.93	2.87	1.46	36.83
Actual	2.42	7.17	26.93	19.18	1.47	57.16
Experi-mental	3.21	7.44	40.28	3.76	2.07	56.76

Spike Pb-contaminated carbonate = 4.02 PPM (for step 2)

Spike Peat Moss (Pb) = 16.31 PPM (for step 4)

Total Spike = 20.33 PPM

Recovery = (56.76-36.83)/20.33x100% = 98.03%

Efficiency = 36.83/37.24 x 100% =98.90%

5.6.4 Speciation and Determination of Cd, Cr, and Pb in Sediments

5.6.4.1 Samples Collection and Storage: In order to determine contamination levels of different site along New Jersey coast, sediment samples were collected from 3 locations: (1) Newark Bay, Newark, NJ (June 1997) (2) South Shore of Shark River estuary, Neptune, NJ (Sep. 08, 1997) (3) Atlantic City Bay, Thekerton, NJ (June 1997). Newark Bay is located in industrial area and sediments are expected to be significantly contaminated by toxic heavy metals. Atlantic City Bay is located in the resort area and sediments are expected to have the lowest level of toxic heavy metals.

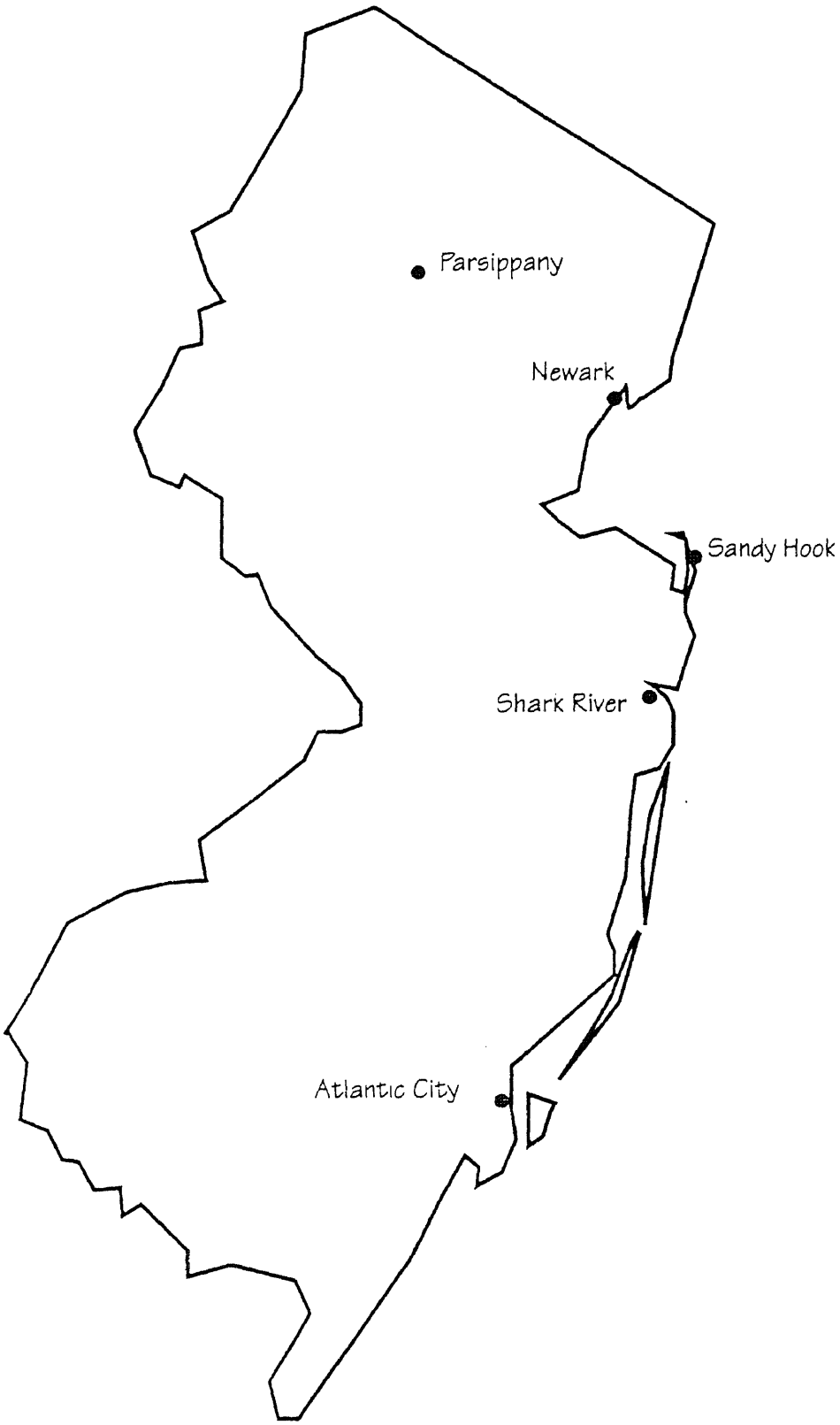
Samples were collected in plastic bags or bottles. At the day of collection, samples were dried overnight in the oven at a 35 $^{\circ}$ C. The dried samples were extracted and analyzed immediately. The remaining samples were stored in sealed plastic bottles at 4 $^{\circ}$ C in a cold room.

Sequential extraction of these sediments using MTM and MWM was carried out for the determination of Cd, Cr, and Pb. Total concentrations of metals were also measured using the EPA total metals method.

5.6.5 Speciation and Determination of Cd, Cr, and Pb in NJ marine Sediments

Sequential extraction of sediments from three different locations were carried out using (1) Modified Tessier Method (MTM), (2) Microwave assisted sequential extraction method (MWM). Microwave acid digestion technique for determination of total metals was also used (See map, next page).

Sampling Sites in New Jersey



5.6.5.1 Total Concentrations of Cd, Cr, and Pb in Sediments: The digested solutions from three locations were analyzed for total concentrations of Cd, Cr, and Pb by GFAAS. Results are presented in Table 5.14 and Figure 5.14.

Table 5.14 Total concentration of Cd, Cr, Pb in the sediment samples from the Newark Bay, Shark River, Atlantic City Bay. n = 3

	Cd		Cr		Pb	
	ppm	%RSD	ppm	%RSD	ppm	%RSD
Newark Bay	1.14	7.89	152.51	5.78	246.15	7.11
Shark River	1.45	5.52	60.55	6.67	78.88	6.86
Atlantic City Bay	1.23	4.88	59.98	5.62	36.93	6.82

It has been demonstrated that total concentrations of Pb and Cr are significantly higher in sediments from the Newark Bay (Table 5.14). Concentration of Pb in sediments from Shark River is about two times higher than in sediments from Atlantic City Bay. Total Cd concentrations are comparable at these sites.

NJDEP soil cleanup criteria (revised 7/11/96) for metals of interest are presented in Table 5.15 and Figure 5.15.

Table 5.15 NJDEP soil cleanup criteria, unit: ppm(w/w)

Element	Residential Area	Nonresidential Area
Cd	1	100
Pb	100	600
Cr(III)	500	500
Cr(VI)	10	10

Concentration of Pb in Newark Bay sediments is significantly higher than cleanup criteria for residential areas. Concentrations of Cd are also somewhat higher than these criteria in all the investigated locations. Cr(VI) concentrations were not measured in sediments because formation of Cr(VI) is not likely in the anaerobic conditions which exist these sediments.

5.6.5.2 Speciation and Determination of Cd in Sediments: Concentration of Cd in different fractions are presented in Table 5.16 with MTM and Table 5.17 with MWM for Newark Bay sediment, Table 5.18 with MTM and Table 5.19 with MWM for Shark River sediment, and Table 5.20 with MTM and Table 5.21 with MWM for Atlantic City Bay sediment. Percent of metals in specific fractions in sediments are presented in Table 5.22.

Table 5.16 Distribution and total Cd in sediment from Newark Bay by MTM , Unit: ppm

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	0.49	0.51	0.56	0.52	7.69	45.61
2) Carbonate	0.04	0.05	0.06	0.05	20.00	4.39
3) Fe/Mn-oxide	0.24	0.24	0.27	0.25	8.00	21.93
4) Organic	0.15	0.15	0.18	0.16	12.50	14.04
5) Residual	0.15	0.16	0.17	0.16	6.25	14.04
Sum 1-5 Cd	1.07	1.11	1.24	**1.14**	7.89	

Table 5.17 Distribution and total Cd in sediment from Newark Bay by MWM, Unit: ppm

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	0.50	0.56	0.59	0.55	9.09	47.41
2) Carbonate	0.036	0.041	0.043	0.04	10.00	3.45
3) Fe/Mn-oxide	0.27	0.27	0.30	0.28	7.14	24.14
4) Organic	0.13	0.14	0.15	0.14	7.14	12.07
5) Residual	0.14	0.148	0.162	0.15	6.67	12.93
Sum 1-5 Cd	1.076	1.159	1.245	**1.16**	6.90	
EPA Total Cd	1.07	1.11	1.24	**1.14**	7.89	

Table 5.18 Distribution and total Cd in sediment from Shark River by MTM
Unit: ppm (w/w)

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	0.71	0.75	0.82	0.76	7.89	52.78
2) Carbonate	0.037	0.039	0.044	0.04	10.00	2.78
3) Fe/Mn-oxide	0.28	0.28	0.31	0.29	6.90	20.14
4) Organic	0.27	0.29	0.31	0.29	6.90	20.14
5) Residual	0.05	0.06	0.07	0.06	16.67	4.17
Sum 1-5 Cd	1.347	1.419	1.554	**1.44**	7.64	

Table 5.19 Distribution and total Cd in sediment from Shark River by MWM, Unit: ppm (w/w)

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	0.70	0.73	0.76	0.73	4.11	49.32
2) Carbonate	0.037	0.039	0.044	0.04	10.00	2.70
3) Fe/Mn-oxide	0.54	0.56	0.63	0.57	8.77	38.51
4) Organic	0.085	0.089	0.096	0.09	6.67	6.08
5) Residual	0.045	0.05	0.055	0.05	10.00	3.38
Sum 1-5 Cd	1.407	1.468	1.585	**1.48**	6.08	
EPA Total Cd	1.38	1.44	1.53	**1.45**	5.52	

Table 5.20 Distribution and total Cd in sediment from Atlantic City Bay by MTM, Unit: ppm (w/w)

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	0.55	0.57	0.62	0.58	6.90	48.33
2) Carbonate	0.045	0.05	0.055	0.05	10.00	4.17
3) Fe/Mn-oxide	0.42	0.44	0.49	0.45	8.89	37.50
4) Organic	0.07	0.08	0.09	0.08	12.50	6.67
5) Residual	0.036	0.039	0.045	0.04	12.50	3.33
Sum 1-5 Cd	1.121	1.179	1.30	**1.20**	7.50	

Table 5.21 Distribution and total Cd in sediment from Atlantic City Bay by MWM, Unit: ppm (w/w)

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	0.47	0.52	0.54	0.51	7.84	41.13
2) Carbonate	0.038	0.04	0.042	0.04	5.00	3.23
3) Fe/Mn-oxide	0.56	0.58	0.63	0.59	6.78	47.58
4) Organic	0.055	0.06	0.065	0.06	8.33	4.84
5) Residual	0.036	0.04	0.044	0.04	10.00	3.23
Sum 1-5 Cd	1.159	1.24	1.321	**1.24**	6.53	
EPA Total Cd	1.18	1.22	1.29	**1.23**	4.88	

Table 5.22 Comparison of Cd in different sediment fractions (Figure 5.16)

	Newark Bay Fraction%		Shark River Fraction%		Atlantic City Bay Fraction%	
	MWM	MTM	MWM	MTM	MWM	MTM
Exchangeable	47.41	45.61	49.32	52.78	41.13	48.33
Carbonate	3.45	4.39	2.70	2.78	3.23	4.17
Fe/Mn-oxide	24.14	21.93	38.51	20.14	47.58	37.50
Organic matter	12.07	14.04	6.08	20.14	4.84	6.67
Residual	12.93	14.04	3.38	4.17	3.23	3.33

Data for Cd using MWM and MTM are reasonably close in each fraction for all locations, especially in the exchangeable and carbonate fractions.

It is found that 40-50% of Cd in all investigated marine sediments exists in the most dangerous, exchangeable form. Total concentration of Cd is higher than cleanup criteria for residential areas in all these sediments.

Surprisingly, Cd total concentrations and distribution between different fractions are similar for sediments from the industrial Newark area and resort Atlantic City Bay area, and are also high in the Shark River, a residential area.

Exchangeable Cd levels of 0.5-0.7 ppm in the resort area (Atlantic City Bay) seem to be excessive and further investigations may be needed in order to determine Cd levels in New Jersey sediments and discuss measures for Cd pollution prevention.

Speciation of Cd in several industrial and agriculture locations in the mouth of Ebro River (North Spain) has been recently reported by Ramos et al [83]. Comparison of our results and these data are presented in Table 5.23. The exchangeable fraction dominates the distribution in sediments and a significant amount of Cd was also found in the acid reducible fraction. Distribution of Cd in sediments from different parts of the world is quite similar. The high content of Cd in the exchangeable form agreed with earlier published results [81], and can be explained by the low stability of cadmium carbonate and low stability of the complexes formed with the organic matter.

5.6.5.3 Speciation and Determination of Cr in Sediments: Concentrations of Cr in different fractions are presented in Table 5.24 by MTM and Table 5.25 by MWM for Newark Bay sediment. Table 5.26 by MTM , Table 5.27 by MWM for Shark River

sediment, and Table 5.28 by MTM and Table 5.29 by MWM for Atlantic City Bay sediment. Percent of specific fraction in sediment are presented in Table 5.30.

Table 5.23 Comparison of Cd distribution in NJ and Northeast Spain sediments

	% of total Cd in fraction New Jersey Sample N=6	% of total Cd in fraction Ebro River (Spain) Sample N=7
Exchangeable (F1)	41-50	
Carbonate (F2)	2-4	52-78 (F1+F2)
Fe/Mn-oxide (F3)	20-48	22-34
Organic (F4)	4-20	0-5
Residual (F5)	3-14	0-11

Table 5.24 Distribution and total Cr in sediment from Newark Bay by MTM, Unit: ppm

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	2.37	2.45	2.77	2.53	8.30	1.84
2) Carbonate	6.21	6.54	7.11	6.62	6.95	4.81
3) Fe/Mn-oxide	52.69	56.34	61.31	56.78	7.63	41.28
4) Organic	50.99	54.80	58.34	54.71	6.73	39.77
5) Residual	15.77	16.88	18.11	16.92	6.91	12.30
Sum 1-5 Cr	128.03	137.01	147.64	**137.56**	7.14	

Table 5.25 Distribution and total Cr in sediment from Newark Bay by MWM

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	3.15	3.29	3.55	3.33	6.01	2.19
2) Carbonate	2.21	2.45	2.66	2.44	9.43	1.61
3) Fe/Mn-oxide	80.67	84.98	90.88	85.51	6.00	56.26
4) Organic	35.71	38.57	42.12	38.80	8.27	25.53
5) Residual	20.01	21.88	23.84	21.91	8.76	14.42
Sum 1-5 Cr	141.75	151.17	163.05	**151.99**	7.02	
EPA Total Cr	144.15	151.67	161.71	**152.51**	5.78	

Table 5.26 Distribution and total Cr in sediment from Shark River by MTM
Unit: ppm (w/w)

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	0.79	0.85	0.94	0.86	9.30	1.52
2) Carbonate	3.89	4.11	4.30	4.10	5.12	7.25
3) Fe/Mn-oxide	15.07	16.29	17.55	16.30	7.61	28.82
4) Organic	24.61	26.60	28.50	26.57	7.34	46.98
5) Residual	7.98	8.69	9.52	8.73	8.82	15.43
Sum 1-5 Cr	52.34	56.54	60.81	**56.56**	7.50	

Table 5.27 Distribution and total Cr in sediment from Shark River by MWM
Unit: ppm (w/w)

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	1.44	1.53	1.65	1.54	7.14	2.55
2) Carbonate	1.35	1.47	1.56	1.46	7.53	2.42
3) Fe/Mn-oxide	16.10	16.99	17.76	16.95	4.90	28.06
4) Organic	18.11	19.68	21.58	19.79	8.79	32.76
5) Residual	18.97	20.77	22.27	20.67	7.98	34.22
Sum 1-5 Cr	55.97	60.44	64.82	**60.41**	7.33	
EPA Total Cr	57.10	59.55	65.00	**60.55**	6.67	

Table 5.28 Distribution and total Cr in sediment from Atlantic City Bay
by MTM, Unit: ppm (w/w)

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	0.89	0.95	1.04	0.96	8.33	1.78
2) Carbonate	2.67	2.87	3.10	2.88	7.64	5.35
3) Fe/Mn-oxide	15.38	16.65	17.89	16.64	7.57	30.88
4) Organic	19.39	20.54	21.66	20.53	5.55	38.11
5) Residual	12.09	12.88	13.64	12.87	6.06	23.89
Sum 1-5 Cr	50.42	53.89	57.33	**53.88**	6.42	

Table 5.29 Distribution and total Cr in sediment from Atlantic City Bay by MWM
Unit: ppm (w/w)

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	1.32	1.47	1.53	1.44	7.64	2.39
2) Carbonate	1.67	1.69	1.83	1.73	5.20	2.87
3) Fe/Mn-oxide	22.51	24.50	25.26	24.09	5.89	40.02
4) Organic	17.69	18.46	19.92	18.69	6.05	31.05
5) Residual	13.25	14.29	15.18	14.24	6.81	23.66
Sum 1-5 Cr	56.44	60.41	63.72	**60.19**	6.05	
EPA Total Cr	56.66	59.89	63.39	**59.98**	5.62	

Table 5.30 Distribution of Cr in different sediment fractions (Figure 5.17)

	Newark Bay		Shark River		Atlantic City Bay	
	Fraction%		Fraction%		Fraction%	
	MWM	MTM	MWM	MTM	MWM	MTM
Exchangeable	2.19	1.84	2.55	1.52	2.39	1.78
Carbonate	1.61	4.81	2.42	7.25	2.87	5.35
Fe/Mn-oxide	56.26	41.28	28.06	28.82	40.02	30.88
Organic matter	25.53	39.77	32.76	46.98	31.05	38.11
Residual	14.42	12.30	34.22	15.43	23.66	23.89

Concentration of exchangeable Cr in all sediment samples is low (1.5-2.5%). Concentration of carbonate bound Cr is also not high (4-7%). Typically, MWM gives somewhat higher exchangeable concentration and somewhat lower carbonate bound concentration. The majority of Cr is distributed in Fe/Mn-oxide (30-56%), organic matter (30-50%), and residual fractions (12-35%). Data from MWM and MTM for Cr are reasonably close. In spite of rather high total Cr concentration in Newark Bay sediments, the sum of exchangeable and carbonate bound fraction is not more than 7%. So, Cr from this and other area is strongly bound to sediments and is not substantially leachable in ordinary environmental conditions.

Distribution of Cr in NJ marine sediments can be compared with Cr speciation in Huelva Estuary sediments from Southern Spain [72] (Table 5.31). Three different sequential extraction procedures: Tessier Method [3], Kerstein Method [67], and BCR method were compared by Spanish researchers [65]. Results were similar for acid reducible fractions and somewhat different in other fractions. The range of Cr distribution in different Huelva Estuary sediments when Tessier Method were used presented in Table. Although Cr distribution in the last three fractions is quite different, both NJ and Spanish sediments contain low concentrations of the environmentally important exchangeable and carbonate bound fractions. Trivalent Cr is usually strongly bound with soil and sediment particles and is not prone to leach in the environment unless more dangerous and soluble Cr(VI) species are formed (Table 5.31).

Table 5.31 Comparison of Cr distribution in NJ and Huelva Estuary (Spain) sediments [72]

	% of total Cr in fraction New Jersey Sample N=6	% of total Cr in fraction Huelva Estuary Sample N=4
Exchangeable	1-3	0.4-2
Carbonate	1-7	0.6-1
Fe/Mn-oxide	28-57	3-12
Organic	26-47	0.5-2
Residual	12-34	84-95

5.6.5.4 Speciation and Determination of Pb in Sediment: Concentrations of Pb in different fractions found in three marine sediments are presented in Table 5.32 by MTM and Table 5.33 by MWM for Newark Bay sediments. Table 5.34 by MTM and Table 5.35 by MWM for Shark River sediments, and Table 5.36 by MTM and Table 5.37 by MWM for Atlantic City Bay sediments. Percent of specific fraction in sediments are presented in Table 5.38.

Table 5.32 Distribution and total Pb in sediment from Newark Bay by MTM, Unit: ppm

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	32.79	34.45	36.38	34.54	5.21	14.41
2) Carbonate	56.21	58.96	62.22	59.13	5.09	24.67
3) Fe/Mn-oxide	93.87	97.90	103.40	98.39	4.86	41.05
4) Organic	36.98	39.15	42.01	39.38	6.40	16.43
5) Residual	7.91	8.17	8.58	8.22	4.14	3.43
Sum 1-5 Pb	227.76	238.63	252.59	**239.66**	5.19	

Table 5.33 Distribution and total Pb in sediment from Newark Bay by MWM, Unit: ppm

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	54.17	56.35	62.31	57.61	7.31	23.35
2) Carbonate	42.35	45.27	47.02	44.88	5.26	18.19
3) Fe/Mn-oxide	81.33	85.01	90.25	85.53	5.24	34.66
4) Organic	51.66	54.31	56.09	54.02	4.13	21.89
5) Residual	4.31	4.77	5.02	4.70	7.66	1.90
Sum 1-5 Pb	233.82	245.71	260.69	**246.74**	5.46	
EPA Total Pb	230.60	242.75	265.10	**246.15**	7.11	

Table 5.34 Distribution and total Pb in sediment from Shark River by MTM
Unit: ppm (w/w)

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	1.36	1.47	1.55	1.46	6.85	1.87
2) Carbonate	14.11	15.18	16.16	15.15	6.80	19.40
3) Fe/Mn-oxide	46.38	50.56	55.13	50.69	8.64	64.91
4) Organic	7.65	8.06	8.38	8.03	4.61	10.28
5) Residual	2.58	2.75	2.95	2.76	6.88	3.53
Sum 1-5 Pb	72.08	78.02	84.17	**78.09**	7.75	

Table 5.35 Distribution and total Pb in sediment from Shark River by MWM
Unit: ppm (w/w)

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	2.17	2.33	2.46	2.32	6.47	2.95
2) Carbonate	14.27	15.35	16.40	15.34	6.98	19.48
3) Fe/Mn-oxide	46.95	49.98	53.97	50.30	7.00	63.86
4) Organic	6.56	6.93	7.33	6.94	5.62	8.81
5) Residual	3.57	3.85	4.16	3.86	7.77	4.90
Sum 1-5 Pb	73.52	78.44	84.32	**78.76**	6.87	
EPA Total Pb	73.63	78.57	84.44	**78.88**	6.86	

Table 5.36 Distribution and total Pb in sediment from Atlantic City Bay
by MTM, Unit: ppm (w/w)

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	0.63	0.66	0.72	0.67	7.46	1.91
2) Carbonate	7.02	7.83	8.58	7.81	9.99	22.24
3) Fe/Mn-oxide	17.48	18.70	20.10	18.76	6.98	53.43
4) Organic	5.95	6.46	6.70	6.37	6.01	18.14
5) Residual	1.37	1.51	1.62	1.50	8.67	4.27
Sum 1-5 Pb	32.45	35.16	37.72	**35.11**	7.52	

Table 5.37 Distribution and total Pb in sediment from Atlantic City Bay by MWM, Unit: ppm (w/w)

Sample	I	II	III	Avg.	RSD%	Fraction%
1) Exchangeable	1.88	1.99	2.16	2.01	6.97	5.51
2) Carbonate	6.11	6.63	7.12	6.62	7.70	18.14
3) Fe/Mn-oxide	17.89	18.99	20.00	18.96	5.59	51.95
4) Organic	6.77	7.10	7.19	7.02	3.13	19.23
5) Residual	1.79	1.90	1.98	1.89	5.29	5.18
Sum 1-5 Pb	34.44	36.61	38.45	**36.50**	5.51	
EPA Total Pb	34.39	36.98	39.42	**36.93**	6.82	

Table 5.38 Distribution of Pb in different sediment fractions (Figure 5.18)

Fraction characteristic	Newark Bay Fraction%		Shark River Fraction%		Atlantic City Bay Fraction%	
	MWM	MTM	MWM	MTM	MWM	MTM
Exchangeable	23.35	14.41	2.95	1.87	5.51	1.91
Carbonate	18.19	24.67	19.48	19.40	18.14	22.24
Fe/Mn-oxide	34.66	41.05	63.86	64.91	51.95	53.43
Organic matter	21.89	16.43	8.81	10.28	19.23	18.14
Residual	1.90	3.43	4.90	3.53	5.18	4.27

Exchangeable Pb is low (2-5%) for the less contaminated Shark River and Atlantic City Bay areas, while Newark Bay sediments contain significant concentrations

of exchangeable Pb (23% MWM and 14% MTM). This indicates that anthropogenic pollution in Newark area is substantial and lead contamination is more hazardous that it might be concluded from total Pb concentrations data. For example, the total concentration of lead in sediments is about 3 times higher in Newark Bay than in Shark River, but the concentration of Pb in the more bioavailable exchangeable fraction is more than 10 times higher.

In most cases, concentration found by MWM and MTM gives comparable results. The highest Pb concentrations was found in the third fraction (Fe/Mn-oxide bound).

Our results can be compared with literature data obtained for Pb speciation in two types of marine sediments [72] (Table 5.39). Speciation by BCR method was used for Ebro River sediments and Tessier Method for Huelva Estuary sediments in Spain. In practically all cases, most of the Pb was associated with Fe/Mn-oxide, organic matter, and residual fractions. Sediments from Huelva Estuary have just a trace of exchangeable and carbonate bound lead. However our samples and sediments from Ebro River contain higher concentrations of Pb in the first two fractions. Generally, a less uniform behavior was observed for lead speciation in different sediments than for Cd and Cr. The increase in the levels of the most bioavailable forms of lead is associated with industrial or, specifically, urban activities [83]. This conclusion is confirmed by our data.

Table 5.39 Comparison of Pb distribution in NJ, Ebro River, and Huelva Estuary (Spain) sediments, Unit: % of total metals

	% of total Pb in fraction New Jersey Sample N=6	% of total Pb Ebro River Sample N=7	% of total Pb Huelva Estuary Sample N=4
Exchangeable(F1)	2-23		0.4-1.2
Carbonate (F2)	19-25	8-59 (F1+F2)	1-8
Fe/Mn-oxide (F3)	35-65	0-53	32-64
Organic (F4)	9-22	18-45	8-13
Residual (F5)	2-5	9-47	20-55

5.7 Conclusions on Sediment Speciation

1) Speciation and determination of Cd, Cr, and Pb in marine sediments from three New Jersey locations were carried out by sequential extraction using both MTM and MWM, followed by GFAAS.

2) Kinetics of sequential extraction by MTM and MWM were investigated and procedures for the extraction process were selected.

3) Relative Standard Deviation of MTM and MWM sequential extraction at N=3 was up to 10% for Cr and Pb and up to 15% for Cd. The sum of concentrations in different fractions agreed well with the total metal concentrations in sediments found by EPA method.

4) Trace metal concentrations in different fractions found by the MTM and MWM are close in the most cases. This indicates that the much faster MWM might be used for evaluation of Cd, Cr, and Pb concentrations in specific fractions. More research is

necessary to verify MWM and compare it with traditional sequential extraction procedures using different types of ovens, digestion schedules, and different sediments.

5) Total concentrations of Cr and Pb in marine sediments decreased from the most industrial and polluted Newark area to the South of New Jersey. Total Cd concentrations were found to be similar (1.2-1.5ppm) in sediments from all sites. Total Pb concentrations in sediments from Newark Bay exceeded NJDEP soil clean up criteria for residential areas (100 ppm). Total Cd concentrations in sediments from all sites slightly also exceeded NJDEP soil cleanup criteria for residential areas (1 ppm).

6) It has been found that about 50% of Cd in sediments from all sites was in the exchangeable fraction. This indicates that it can be easily eluted from sediments and is, therefore, more hazardous for aqueous phase and biota.

7) A higher percent of Pb in sediments from Newark Bay exists in the exchangeable fraction than for sediments from other areas. This indicates an anthropogenic character of Pb pollution in this area. For example, total Pb concentration in Newark Bay sediments is about 3 times higher than in Shark River sediments. However, concentration of Pb in exchangeable fraction is more than 10 times higher. It means that sediments from Newark Bay are much more hazardous that it might be concluded from total concentration data alone.

8) Cr concentration in exchangeable and carbonate bound fractions are low (up to 3-7% respectively). In all sediments, it is assumed that the most leachable and dangerous Cr(VI) species are practically absent in the anaerobic conditions in marine sediments.

9) Lead-contaminated carbonate was added to the sediment, and most of it was recovered in the second extraction step. Peat moss was added to the sediment for organic bound lead spike, but most of it was extracted in the first step. The results of the experiment indicate that a material such as peat moss has ion exchange sites as well as stronger binding sites. Total recovery of Pb, including the spiked material, was 98%.

CHAPTER 6

DETERMINATION OF Cd, Cr, AND Pb IN THE SHARK RIVER ECOSYSTEMS INCLUDING NATURAL WATER, SEDIMENTS, AND BIOTA USING MICROWAVE ACID DIGESTION METHOD AND GFAAS

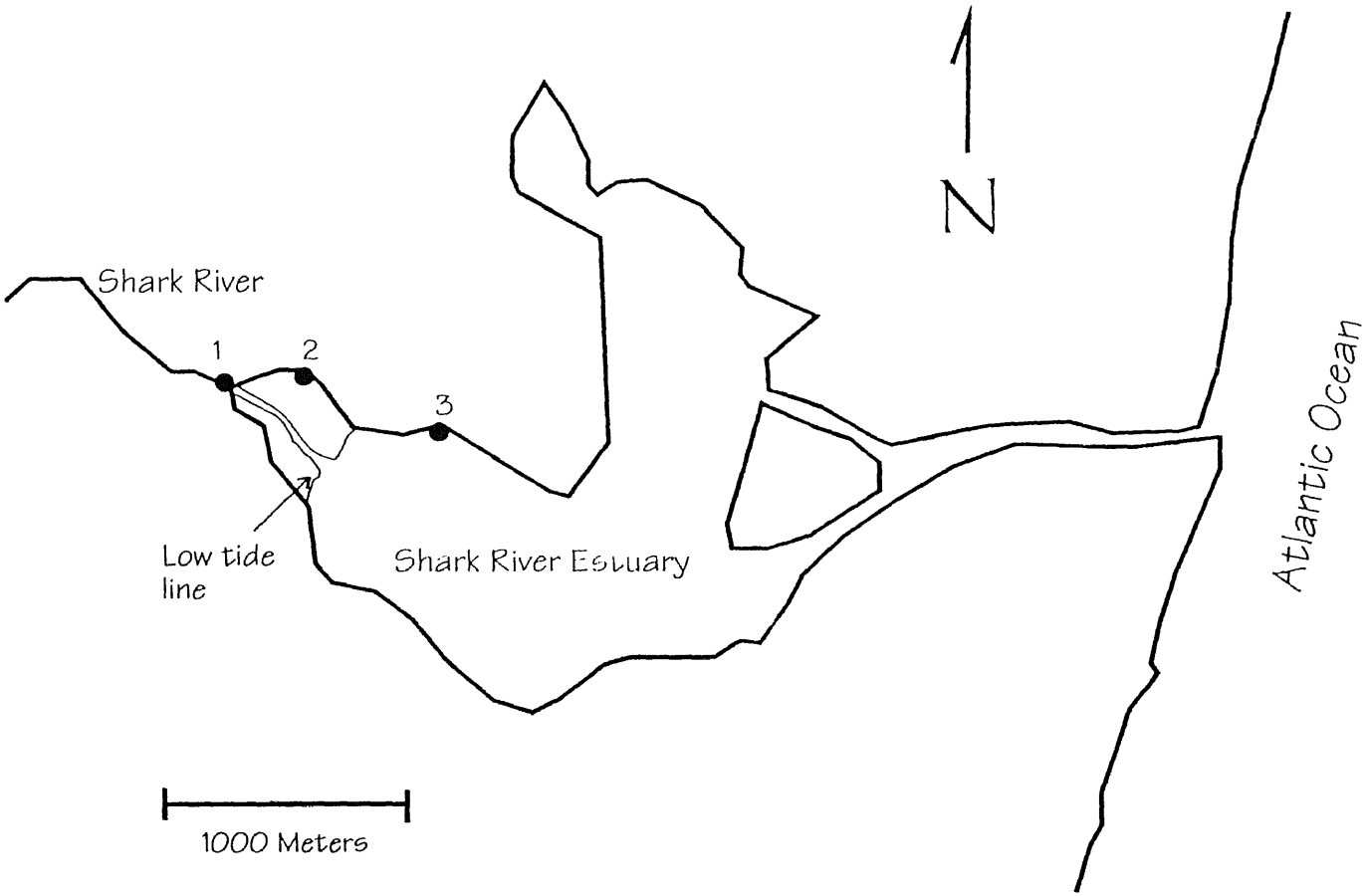
In the final section of this project, Cd, Cr, and Pb were determined in natural water, sediments and different biota samples collected at the same time from three locations in the Shark River (see map, next page).

Concentrations of exchangeable Cd, Cr(III), Cr(VI), and Pb in water samples were found. Speciation and determination of Cd, Cr, and Pb in sediments from three locations were carried out. Total trace metal concentrations in different biota samples including fish, clams, crabs, and plants were also determined.

There was no attempt made to do a complete study on the area. The main purpose of this testing was to apply the developed methods to some environmental samples.

6.1 Samples Collection and Characteristics

Samples of water, sediments, and biota were collected on the south shore of Shark River, NJ, Aug. 18, 1998. (see map) The Shark River is an estuary extending inland approximately 2 miles from Atlantic Ocean, in Neptune and Belmar, NJ. Samples were collected in the most inland area of the southern branch of the estuary. The first site is at the end of the estuary where the Shark River enters it. Site 2 is in a tidal area at the foot of a bluff. This area is under water approximately 50% of the time. The third site is further east toward the


N
Shark River
1
2
3
Low tide
line
Shark River Estuary
Atlantic Ocean
1000 Meters

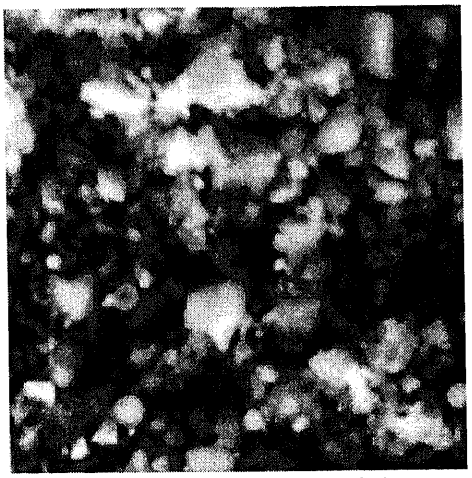
ocean, where the bottom is not exposed at low tide, although the water is only a few feet deep. Sediments in all locations were collected during the low tide period, and site 1 and 2 were not under water. However, during high tides, each day all the sampling sites are covered by water. Plastic bags were filled with water from three sites. pH and salinity of water samples are presented in Table 6.1 and Figure 6.1. The lowest pH and salinity was found at site 1 which is upstream. Sediment samples were collected using a 5 cm diameter tube, samples from the upper 25 cm layer.

Table 6.1 pH and salinity of water samples

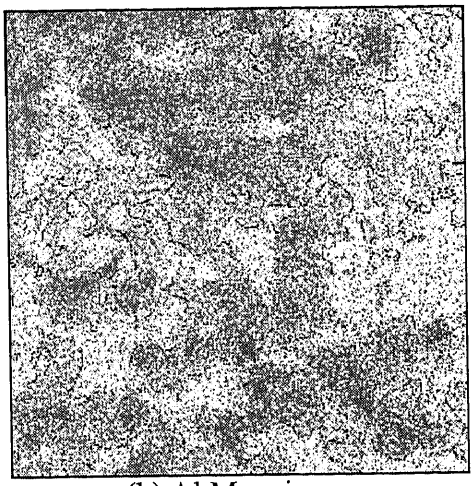
Site	1	2	3
pH	6.80	8.21	8.45
Salinity (g/L or ppt)	1.2	25.10	24.20

Sediment contained more silt and clay at the more upstream sites, and the sand content increased at the site closest to the ocean.

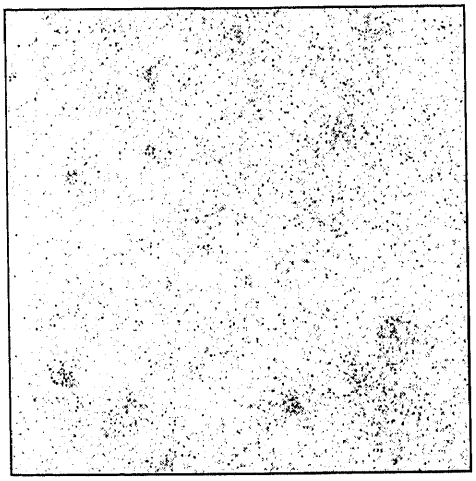
Two types of fish: 9 silverside (Menidia beryllina) and 24 killifish (Fundulus heteroclitus) were collected in the vicinity of sampling sites. Both types of fish were on average 8 cm long. The wet weight of silverside fish was in the range of 2 - 6 grams and killifish in the range of 9 - 17 grams. Three crabs, two blue claw (Callinectes sapidus) and one green crab (Carcinus maenas) were collected in the sampling area. Their wet weight was 11.3, 32.1, and 68.3 grams. Seven clams (Mya arenaria) were also collected. Clams wet



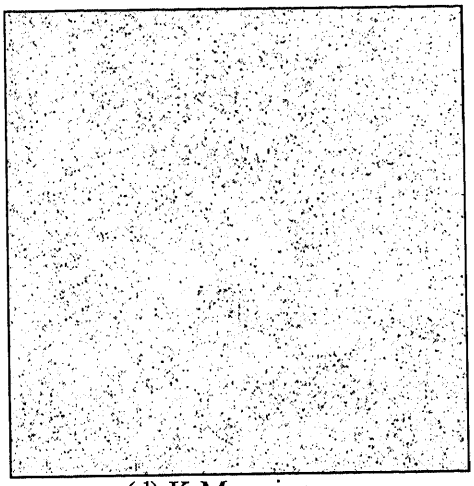
(a) Image of Ground Particles



(b) Al Mapping

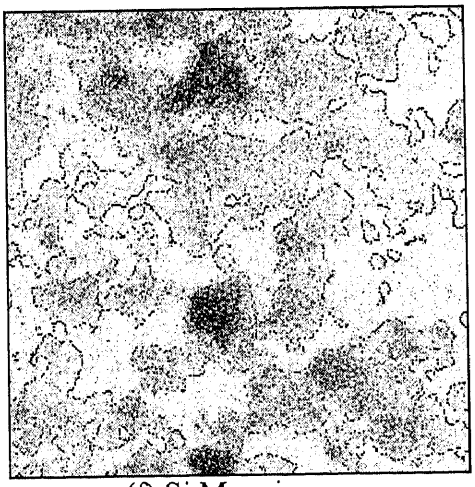


(c) Ca Mapping



(d) K Mapping

(e) Fe Mapping



(f) Si Mapping

Figure 5.54 Elemental Mapping of Ground Particle in Low NO_x Fly Ash (GPU2G), (2150X)

6.3 Results and Discussion

6.3.1 Determination of Cd in Water, Sediments, and Biota

Concentrations of exchangeable Cd in the Shark River water at the investigated locations are presented in Table 6.2 Figure 6.2.

It has been found that Cd concentrations are at a low ppb level and are similar at the three sites.

Table 6.2 Concentration of exchangeable Cd in Shark River water, N=3, Unit: ppb

Site 1		Site 2		Site 3	
Cd	%RSD	Cd	%RSD	Cd	%RSD
1.16	7.76	1.22	8.20	1.67	6.59

Results of Cd speciation and determination in sediments from three locations are presented in Table 6.3 and Figure 6.3.

Table 6.3 Distribution of Cd in sediment from three locations , N = 9, unit: ppm (w/w)

	Site 1			Site 2			Site 3		
	Cd	%RSD	%total	Cd	%RSD	%total	Cd	%RSD	% total
Exchange	1.26	15.8	39.6	0.23	14.8	51.1	0.06	61.4	30.0
Carbonate	0.05	111.4	1.6	0.035	48.6	7.8	0.04	94.7	20.0
Fe/Mn-oxide	1.77	12.4	55.7	0.18	25.1	40.0	0.09	67.4	45.0
Organic	0.16	3.6	5.0	0.003	33.6	0.7	--	--	--
Residual	0.001	152.8	--	0.002	40.4	0.4	0.01	161.7	5.0
Sum 1-5	3.18			0.45			0.20		

Cd concentrations in sediment samples are higher at the upstream site. Sediments at the site 1 are finer and more Cd can be adsorbed from water. The second reason is coagulation of colloid particles containing heavy metals as the increasing salt content causes colloidal coagulation.

Total Cd concentrations in biota samples are presented in Table 6.4 and Figure 6.4..

Table 6.4 Total average concentrations of Cd in biota samples
N = sample number from site 1,2 and 3, unit: ppm (w/w)

Biota	N	Cd, ppm	%RSD
Killifish liver	24	0.12	58.80
Silverside liver	9	0.09	44.44
Clam	6	0.07	42.86
Crab	3	0.33	95.92
Plant	9	0.53	29.60

Concentrations of Cd in fish liver, crabs and clams varied widely from sample to sample. It is known that Cd accumulates in biota and its concentration increases with age. The highest Cd concentration was found in crabs probably because their activities occur in sediments that are more contaminated than water.

6.3.2 Determination of Cr in Water, Sediments, and Biota

Concentrations of exchangeable Cr(III) and Cr(VI) ions in the Shark River water near the investigated locations are presented in Table 6.5.

Table 6.5 Concentrations of exchangeable Cr in Shark River water, N=3, unit: ppm(w/w)

	Site 1		Site 2		Site 3	
	ppm	%RSD	ppm	%RSD	ppm	%RSD
Cr(III)	1.99	4.02	0.99	6.06	0.91	8.79
Cr(VI)	0.63	7.94	0.61	8.20	0.48	6.25
Sum Cr	2.62		1.60		1.39	

The concentrations of Cr(III) are higher at site 1, where the pH is lower, while Cr(VI) concentrations are comparable at all locations. Concentration of the much more toxic Cr(VI) form is less than 1 ppb everywhere.

The results of Cr speciation and determination in sediments from the three locations are presented in Table 6.6 and Figure 6.5.

Cr concentration in sediments is higher at the upstream site. The probable reasons are the finer sediment particle size and coagulation of colloid particles. As with samples investigated in Chapter 5, the Cr concentration in the most leachable exchangeable and carbonate bound forms, is low.

Table 6.6 Distribution of Cr in sediment from three location, N=9, Unit:ppm(w/w)

	Site 1			Site 2			Site 3		
	Cr	%RSD	%total	Cr	%RSD	%total	Cr	%RSD	%total
Exchange	0.06	41.9	0.1	0.06	28.9	0.3	0.04	75.0	0.3
Carbonate	0.46	15.7	1.0	0.46	17.3	2.2	0.28	62.1	2.0
Fe/Mn-oxide	28.48	18.7	62.3	12.66	6.5	60.5	7.82	2.9	56.5
Organic	11.10	31.0	24.3	6.19	29.6	29.6	4.66	23.9	33.7
Residual	5.65	7.2	12.4	1.56	25.0	7.5	1.01	39.9	7.3
Sum 1-5	45.74			20.93			13.81		

Total Cr concentrations in biota samples are presented in Table 6.7.

Table 6.7 Total average concentrations of Cr in biota samples
N = sample number from site 1,2 and 3, unit: ppm (w/w)

Biota	N	Cr, ppm	%RSD
Killifish liver	24	0.11	43.22
Silverside liver	9	1.25	21.41
Clam	6	1.33	42.11
Crab	3	1.43	62.80
Plant	9	3.07	93.76

6.3.3 Determination of Pb in Water, Sediments, and Biota

Concentrations of exchangeable Pb in the Shark River water near the investigated locations are presented in Table 6.8.

Table 6.8 Concentration of exchangeable Pb in Shark River water, N=3, Unit: ppm (w/w)

Site 1		Site 2		Site 3	
Pb	%RSD	Pb	%RSD	Pb	%RSD
3.22	8.07	2.29	6.99	1.75	6.93

As for other metals, the highest Pb concentration was found in water from site 1. However, Pb concentration at all locations is lower than the threshold concentration for drinking water.

Results of Pb speciation and determination in sediments from three locations are presented in Table 6.9 and Figure 6.7.

Pb concentration in sediments is much higher at site 1. This is also true for Cd and Cr. We mentioned that sediments from Site 1 are finer. It means that the adsorption ability is higher. The second reason might be coagulation and deposition of colloid particles with increasing electrolytes level as the river, water mixes with salt water.

Table 6.9 Distribution of Pb in sediment from three locations
N = 9, unit: ppm (w/w)

	Site 1			Site 2			Site 3		
	Pb	%RSD	%total	Pb	%RSD	%total	Pb	%RSD	%total
Exchange	0.67	91.4	1.3	0.56	28.5	5.9	1.00	27.2	10.7
Carbonate	7.09	26.3	13.8	1.92	48.4	20.2	0.47	109.6	5.0
Fe/Mn-oxide	40.71	4.9	79.4	5.47	1.9	57.6	6.15	17.5	65.6
Organic	1.58	4.4	3.1	0.82	13.4	8.6	1.06	25.6	11.3
Residual	1.23	7.8	2.4	0.72	5.8	7.6	0.69	40.2	7.4
Sum 1-5	51.28			9.50			9.37		

Total Pb concentration in biota are presented in Table 6.10.

Table 6.10 Total average concentrations of Pb in biota samples
N = sample number from site 1,2 and 3, unit: ppm (w/w)

	N	Pb, ppm	%RSD
Killifish liver	24	0.07	99.51
Silverside liver	9	2.67	33.33
Clam	6	0.39	41.03
Crab	3	0.91	54.22
Plant	9	3.17	91.73

Quite different Pb concentrations were found in livers of killifish and silverside. Apparently, concentrations of heavy metals vary significantly for different species and for different individual specimens.

6.3.4 Relationship Between Trace Metal Concentrations in Water, and Sediments

From concentrations of trace metals in water and sediments presented in Chapter 6.3.1, 6.3.2, and 6.3.3, the ratios were found. Results for Cd, Cr and Pb are presented in Table 6.11 , 6.12, an 6.13 respectively.

It can be concluded that the ratios between total concentrations in sediments and concentrations in water are increasing in the order Cr>Pb>Cd. The average ratios found for Cd, Pb, and Cr are 1077, 8266 and 13491 respectively. The reason is that the most leachable exchangeable fraction of Cd in all sediment samples is much higher than of other metals. The lowest exchangeable fraction in sediment was found for Cr. In investigated sediments absolute Cd concentrations are lower than concentrations of Pb and Cr. However, because of Cd high leachability, Cd pollution is more hazardous in the investigated ecosystem and in water samples Cd concentration exceeds the limit for drinking water. Ratios of exchangeable Cr and Pb in sediments to their concentrations in water samples are much lower and more similar for different sites.

Table 6.11 Relationships between total and exchangeable Cd concentrations in sediments and water

Site	sediment(total)/water	sediment(excha)/water
1	2711	1086
2	369	189
3	120	36

Table 6.12 Relationships between total and exchangeable Cr concentrations in sediments and water

Site	sediment(total)/water	sediment(exchange)/water
1	17458	23
2	13081	37
3	9935	29

Table 6.13 Relationships between total and exchangeable Pb concentrations in sediments and water

Site	sediment(total)/water	sediment(exchange)/water
1	15295	208
2	4148	245
3	5354	571

Gonzales et al [81] found that for earthworms Cd exhibits the highest accumulation factor in comparison with other metals (Zn, Pb, Cu) relative to their

concentrations in sediments. It was suggested that for earthworm, the accumulation factor for Cd is governed by the same soil or sediment characteristics that determine equilibrium partition coefficient between the solid state and pore water [76]. Therefore, higher biota/sediment ratios for Cd can be explained by cadmium higher leachability to the water phase. Ramos et al [82] found that Cd concentration in earthworms is close to the concentration in the exchangeable fraction in the sediment.

Studies of bioaccumulation of toxic metals in different biota species are the subject of many investigations and is not the primary goal of this research. However, comparison of Cd, Cr, and Pb concentrations in water, different sediment fractions and in the biota of the specific area might be of the interest for further, more detailed investigations.

6.4 Conclusions on Shark River Ecosystem Samples

1. Concentrations of exchangeable Cd, Cr(III), Cr(VI), and Pb in Shark River water, the distribution of Cd, Cr and Pb in different fractions of sediments from three locations in the Shark River, and concentrations of these metals in biota samples from the river were determined.
2. It was found that concentrations of exchangeable Cd, total Cr and Pb in the water are at a low ppb level. The fraction of Cr(VI) is about 30% of the total exchangeable Cr. Concentrations of Cr and Pb are higher upstream in the Shark River.
3. Total concentrations of the investigated metals in the sediments are higher upstream in the Shark River with maximum concentrations of about 3, 45, and 51 ppm for Cd, Cr and Pb respectively.

4. A significant fraction of Cd in sediments (30-50%) exists in the most leachable, exchangeable, form while for Cr and Pb, the major sediment fraction is bound to Fe/Mn- oxides and only a small part (up to 10% for Pb and up to 1% for Cr) is in the exchangeable form.
5. Concentrations of the investigated metals in biota samples varied significantly for different species and from sample to sample.
6. Relationship between trace metals concentrations in water and sediments were estimated. Ratios between total concentrations in sediments and concentrations in water increase in the order Cr>Pb>Cd. Ratios of exchangeable Cr and Pb in sediments to their concentration in water are much lower and more uniform for the different sites.

CHAPTER 7

CONCLUSIONS

A method for speciation, preconcentration and determination of Cd, Pb, Cr(III) and Cr(VI) in natural waters at the sub-ppb level has been developed. The analytes present in water as ions or unstable complexes are sorbed under static conditions onto fine Chelex-100 or Dowex 1x8 resin beads

In contrast to sorption in a column, sorption on ion exchange beads slurried into a stirred sample provides a homogeneous distribution of the sample on the beads. This allows direct analysis of the beads as a slurry using GFAAS.

Speciation and preconcentration of trace metals can be carried out on-site, using these ion exchange materials. The sample-loaded ion exchange matrix can be separated from the water sample for delivery to the analytical laboratory. This eliminates the possibility of changes in the form of the analytes which can occur during water sample storage.

It is shown that the sample-loaded resin can be stored either dry, or suspended in a small quantity of the eluting acid solution, allowing determinations to be done in the future, for legal or other purposes.

Lead, cadmium and chromium concentrations in tap water and in several natural water samples were determined. Some difference was found between the 'dissolved' lead and cadmium determined after filtration and acidification of the sample, and the

'exchangeable' metals, measured using the method developed in the current work. Speciation of the chromium content between Cr(VI) and Cr(III) was also demonstrated, using this method, a distinction which is impossible if total dissolved metals is determined using the EPA method.

Speciation and determination of Cd, Cr and Pb in marine sediments from three New Jersey locations were carried out by sequential extraction using Modified Tessier method (MTM) and Microwave method (MWM), followed by GFAAS. Trace metal concentrations in different fractions are close in the most cases. This indicates that the much faster MWM might be used for evaluation of Cd, Cr and Pb concentrations in specific fractions. Total concentrations and exchangeable fractions of Cr and Pb decreased from the most industrial Newark areas to the south of New Jersey. Cd concentrations were found to be similar in all locations.

Concentrations of exchangeable Cd, Cr(III), Cr(VI) and Pb in Shark River water, the distribution of Cd, Cr and Pb in different fractions of sediments from three locations in the Shark River, and concentrations of these metals in biota samples from the river were determined.

Relationship between investigated trace metals concentrations in water sediments and biota were estimated. Ratios between total concentrations in sediments and concentrations in water increase in the order Cr>Pb>Cd. Ratios of exchangeable Cr and Pb in sediments to their concentration in water are much lower and more uniform for the different sites.

APPENDIX A - FIGURES FOR CHAPTER 4

METHOD DEVELOPMENT AND VALIDATION FOR PRECONCENTRATION, SPECIATION, AND DETERMINATION OF DISSOLVED HEAVY METALS IN WATER

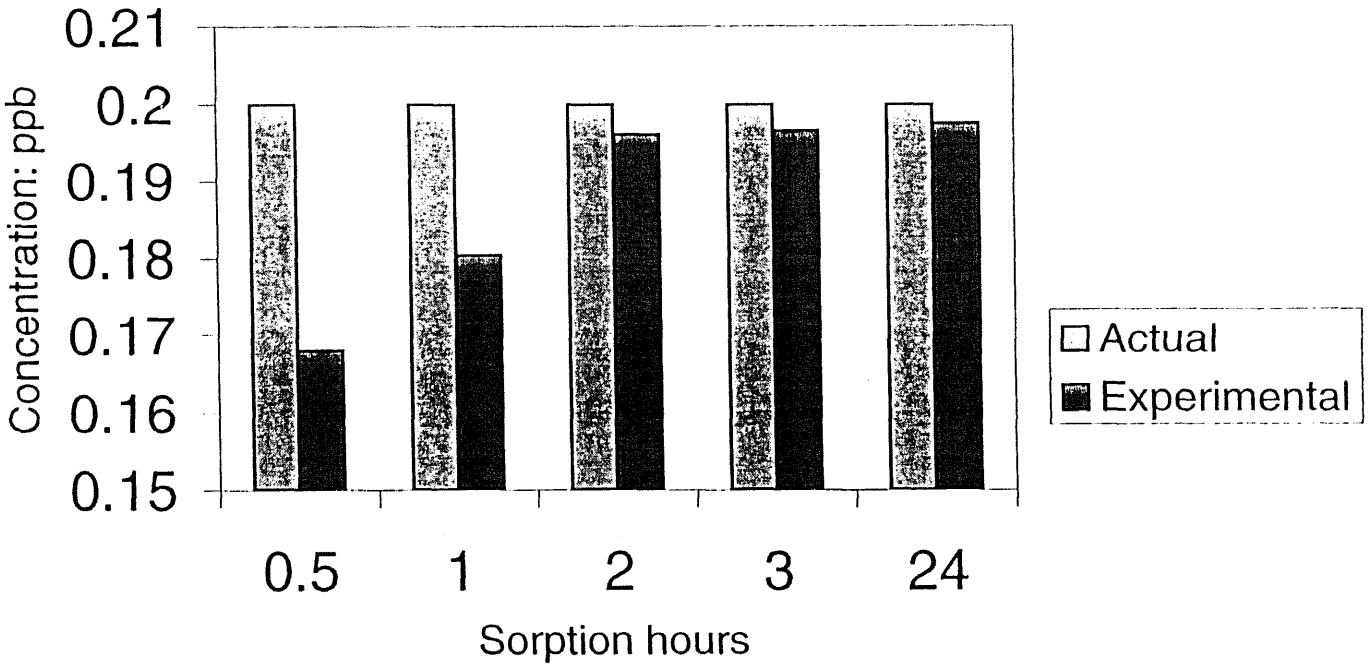


Figure 4.1 Kinetics of sorption of Cd on Chelex 100

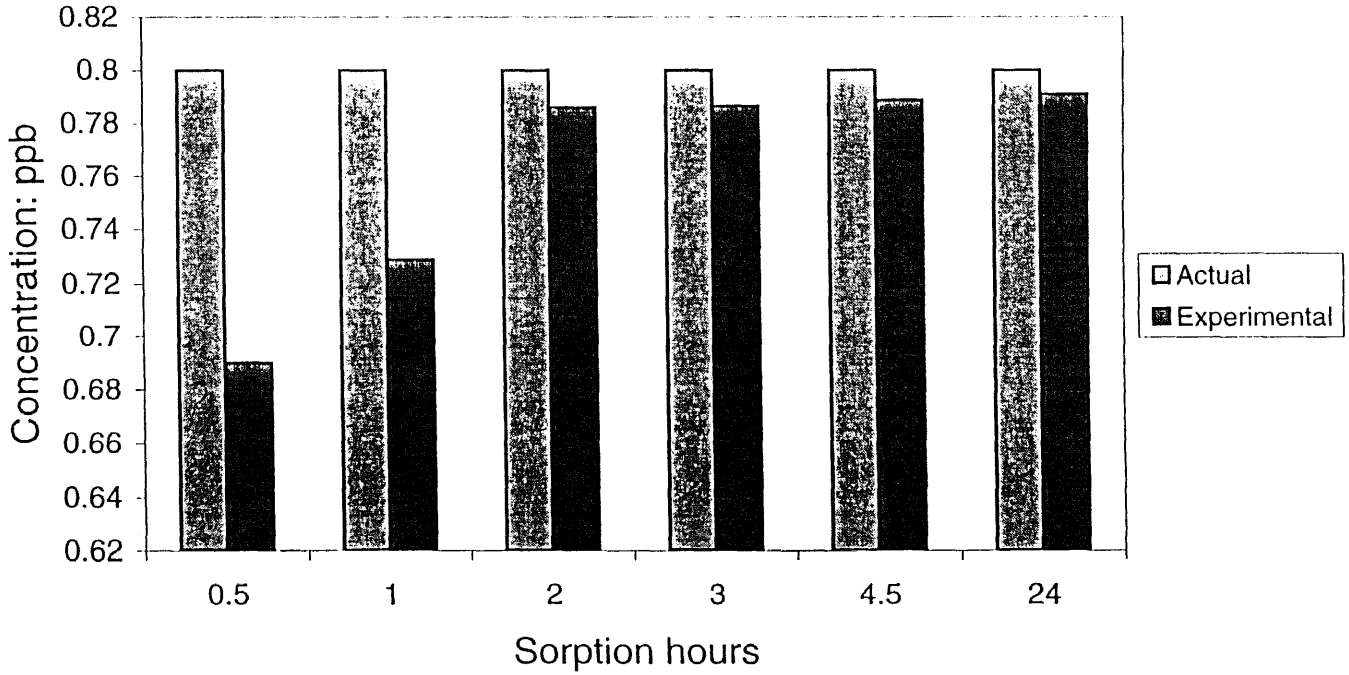


Figure 4.2 Kinetics of sorption of Cr(VI) on Dowex1x8

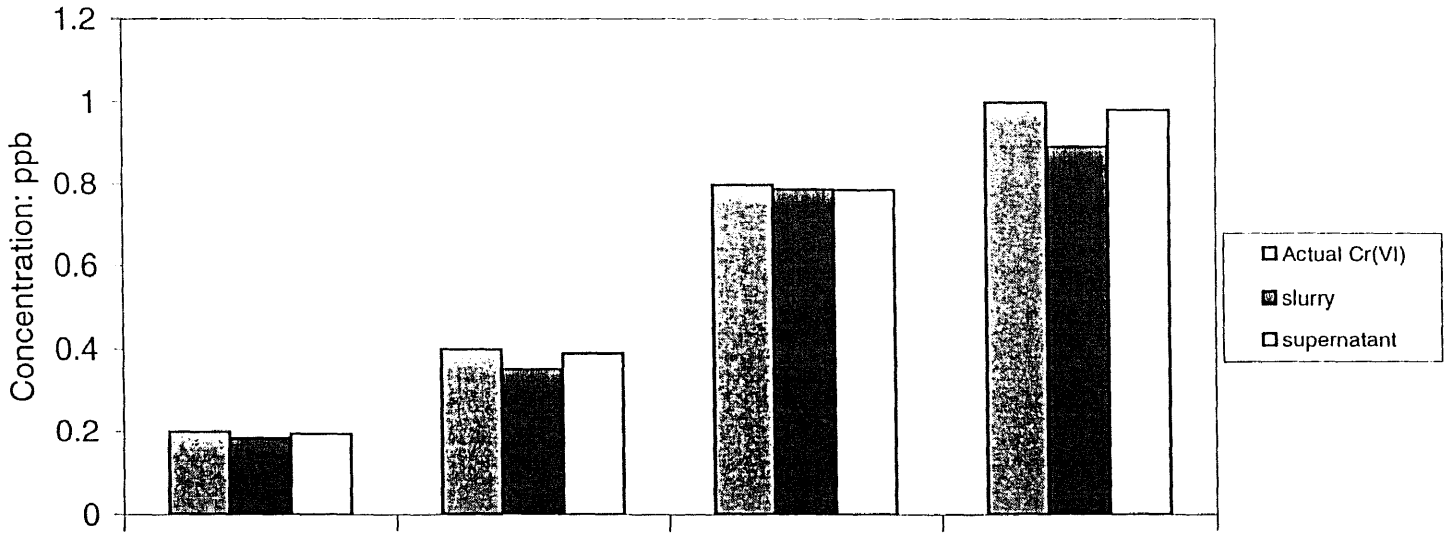


Figure 4.3 Comparison of slurry and supernatant analysis methods on Cr(VI)

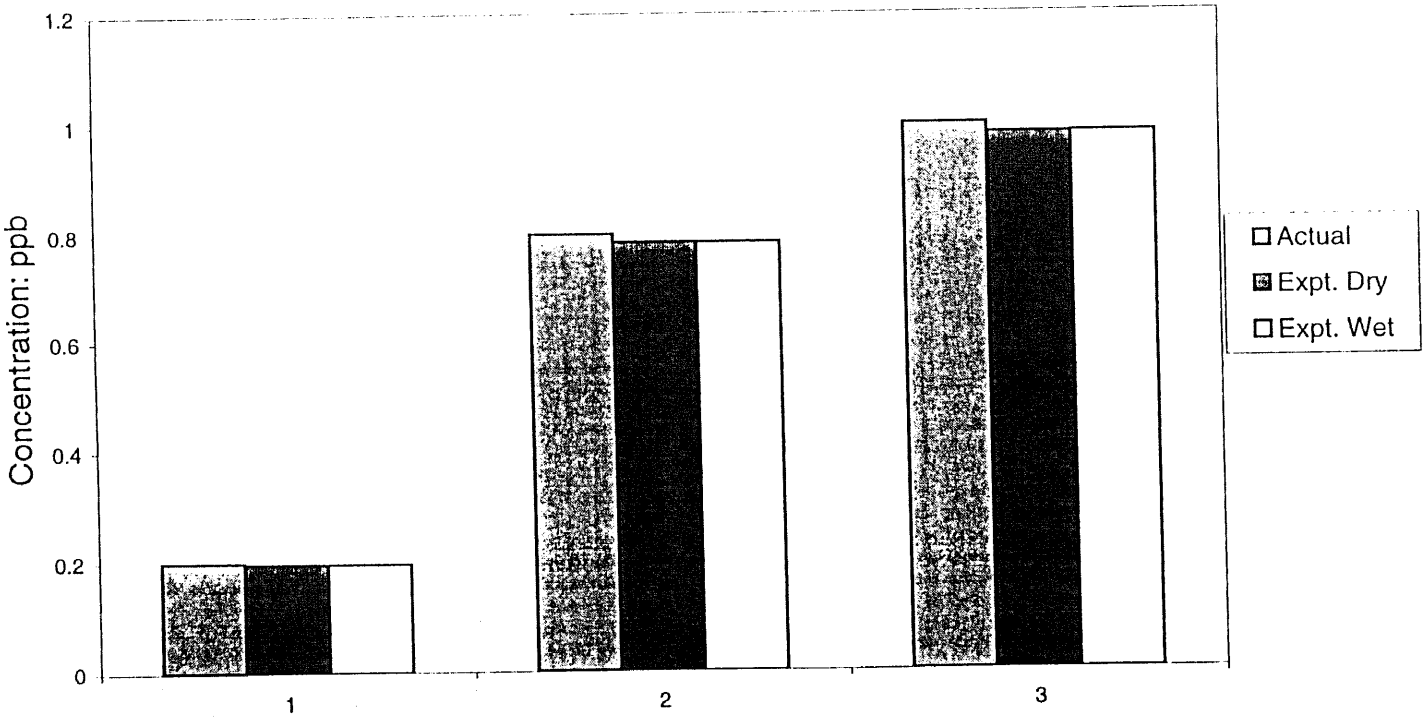


Figure 4.4 Three weeks Dry and Wet storage on Pb

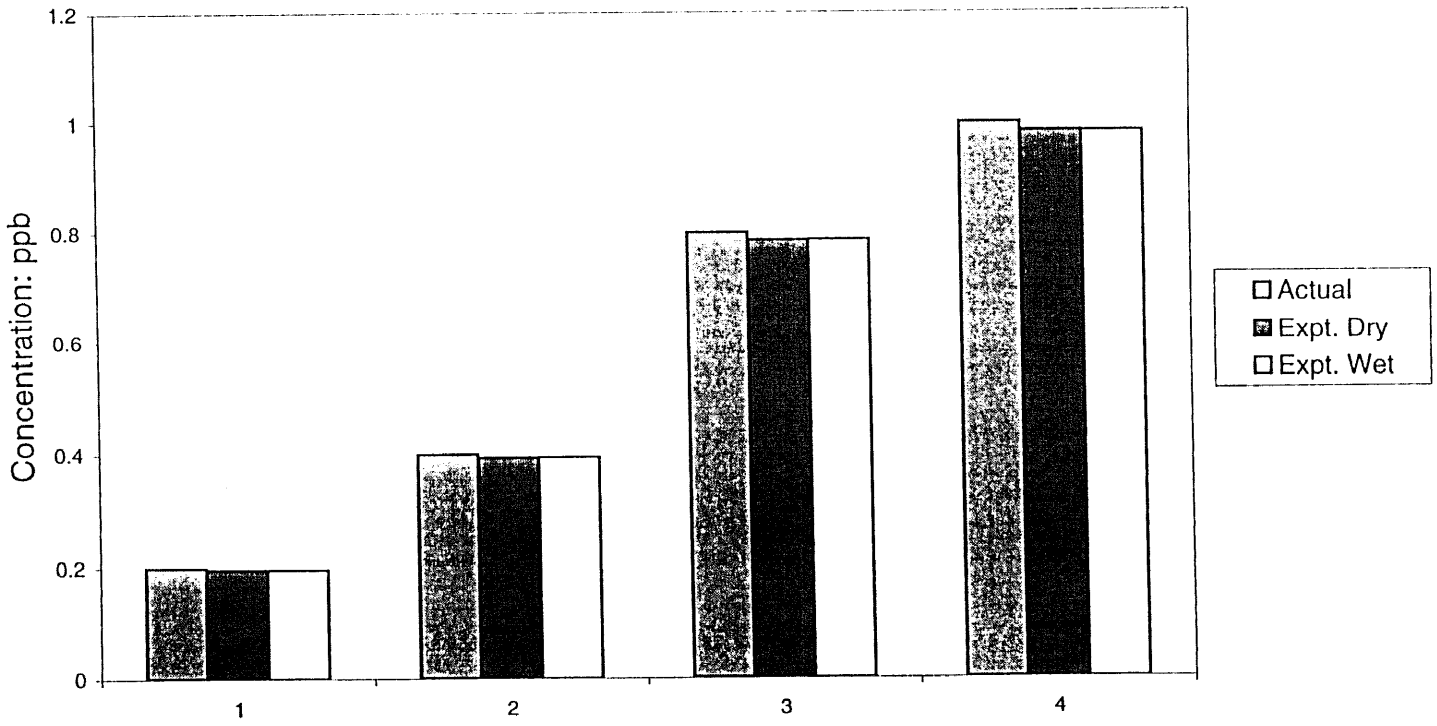


Figure 4.5 Three weeks Dry and Wet storage on Cd

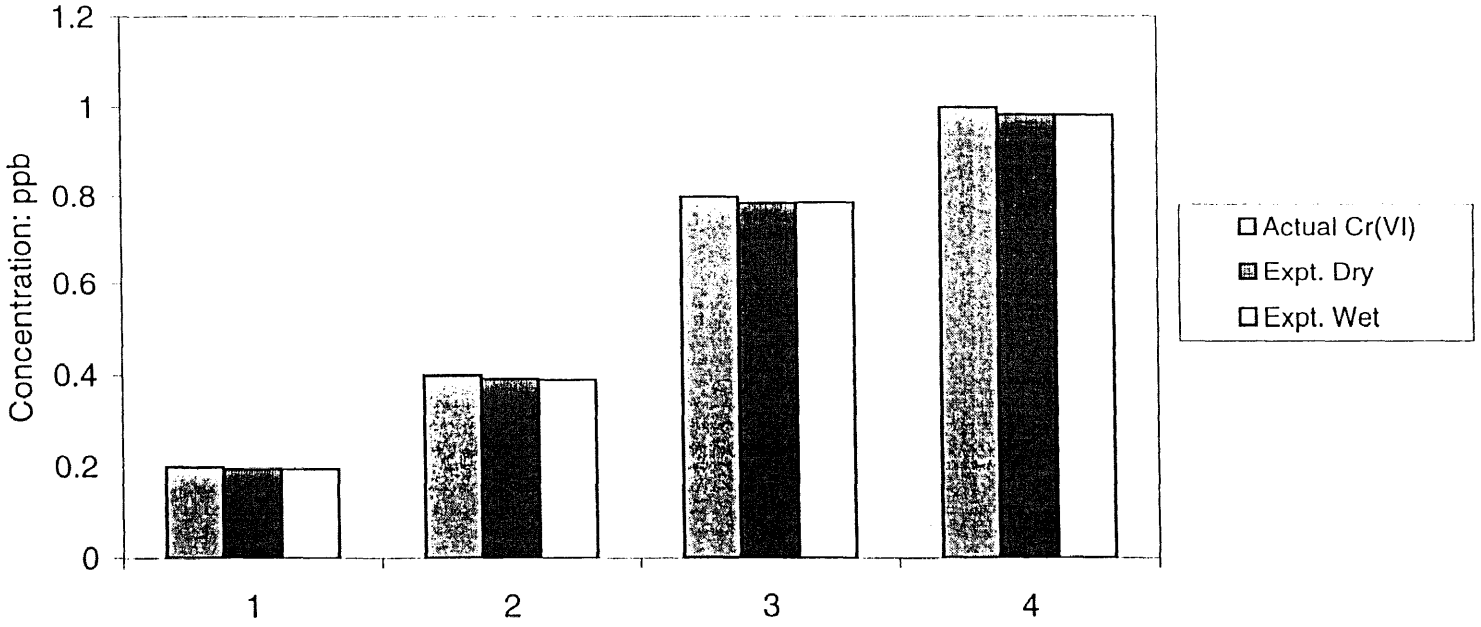


Figure 4.6 Three weeks Dry and Wet storage on Cr(VI)

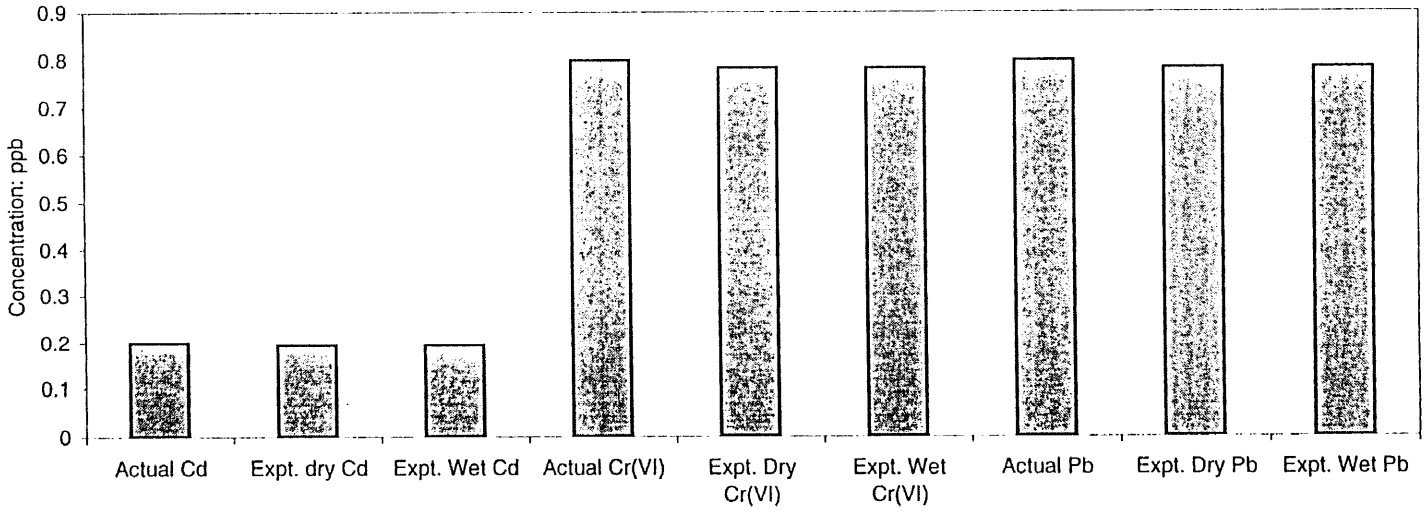


Figure 4.7 Five months Dry and Wet storage on Cd, Cr(VI),Pb

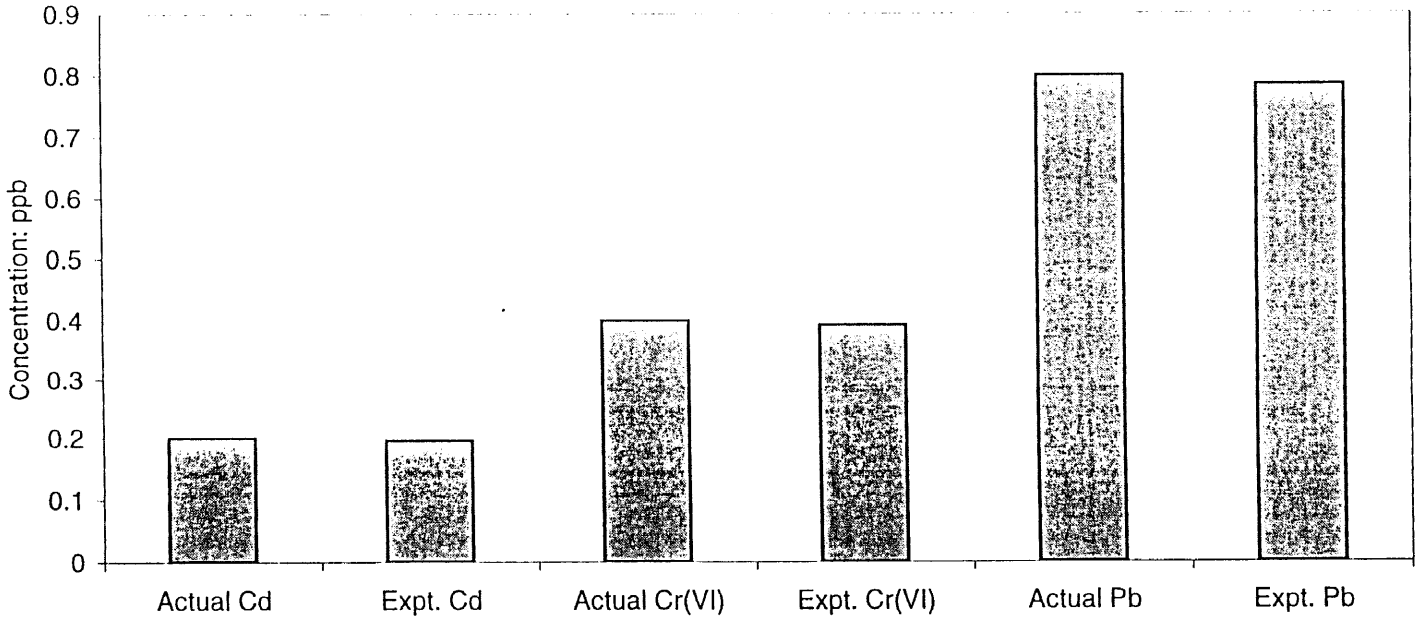


Figure 4.8 Recovery study for Cd, Cr(VI), Pb standards

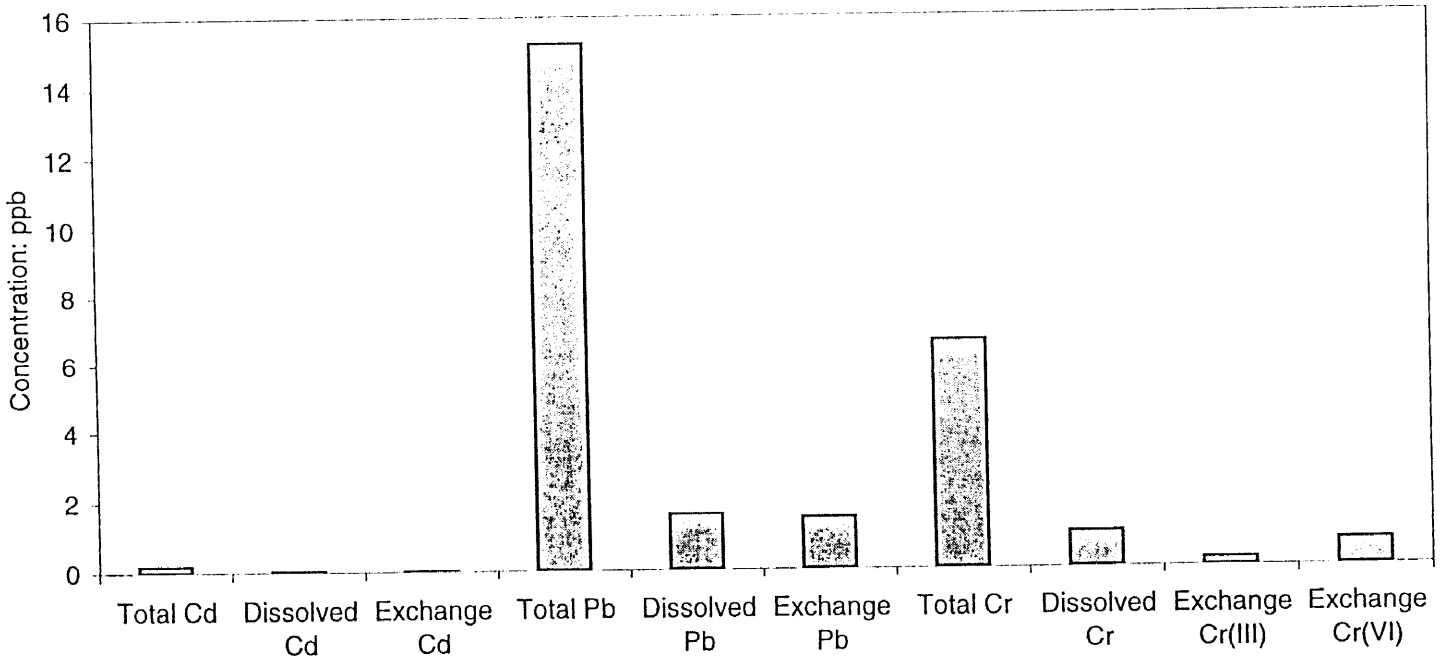


Figure 4.9 Total, Dissolved, and Exchangeable Cd, Pb, Cr(III), Cr(VI) in Passaic River water

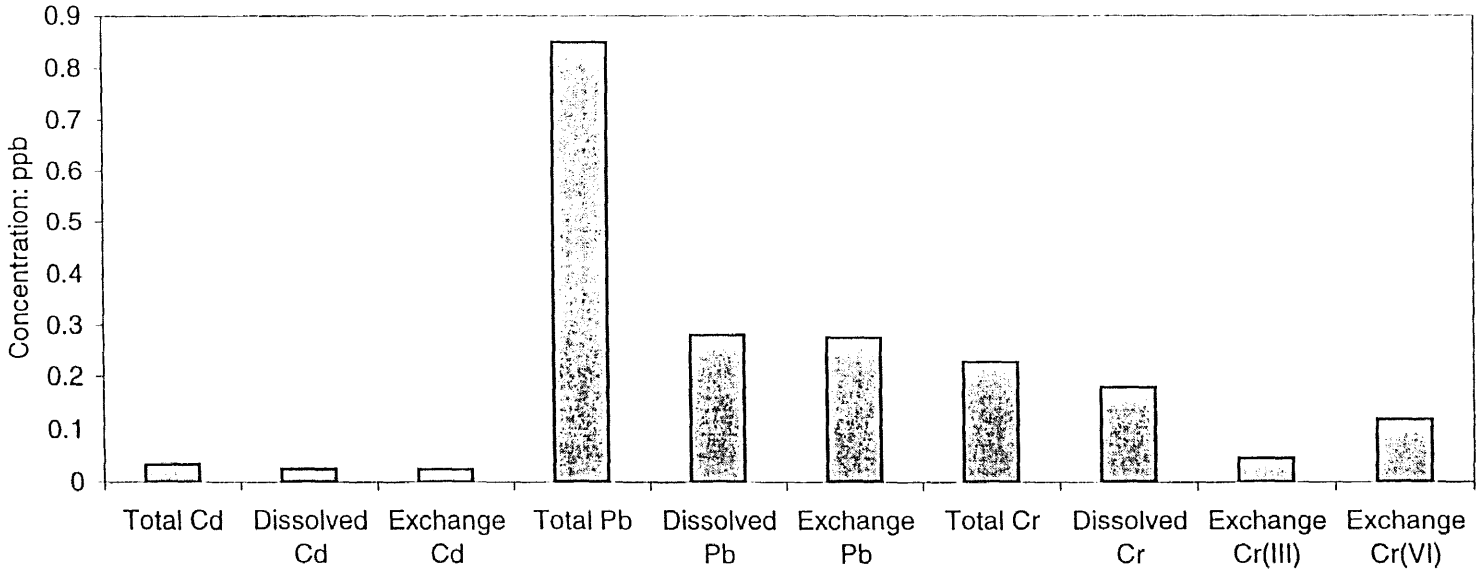


Figure 4.10 Total, Dissolved, and Exchangeable Cd, Pb, Cr(III), Cr(VI) in Parsippany Lake water

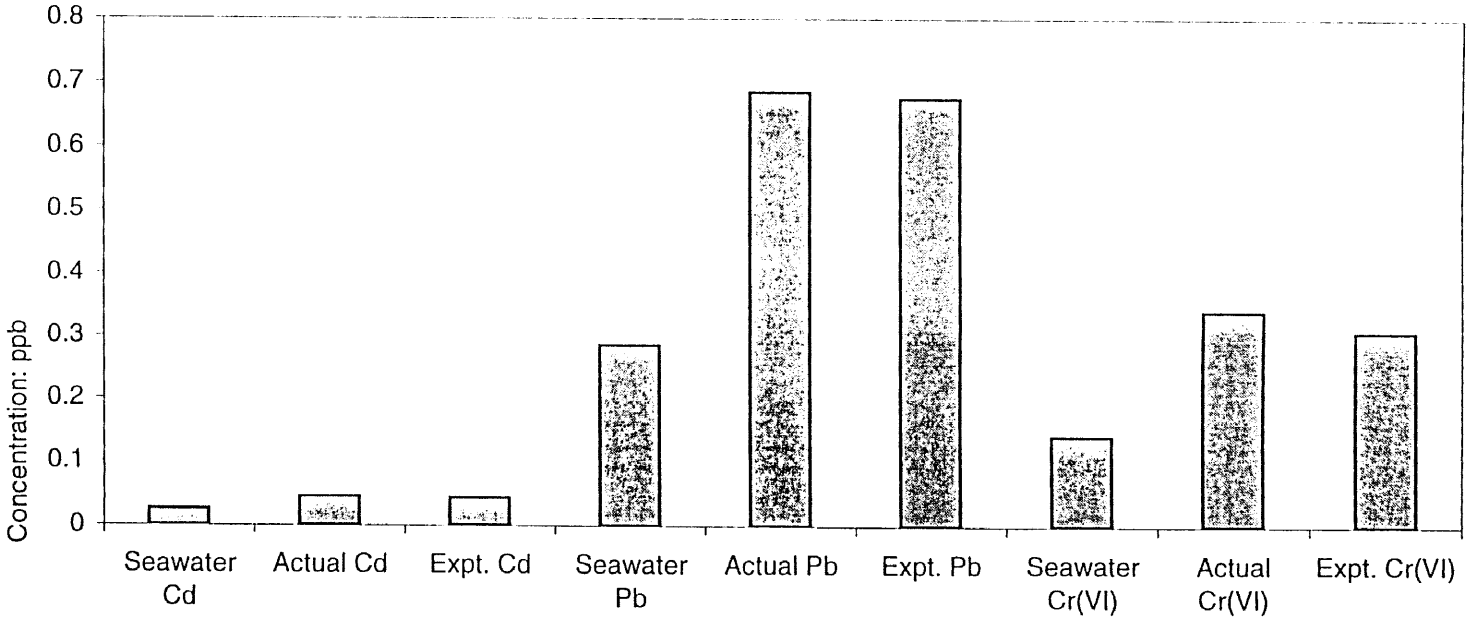


Figure 4.11 Recovery study of Cd, Pb, Cr(VI) from fortified seawater samples

APPENDIX B - FIGURES FOR CHAPTER 5

SPECIATION OF TRACE ELEMENTS IN SEDIMENT USING SEQUENTIAL SELECTIVE EXTRACTANTS AND GFAAS

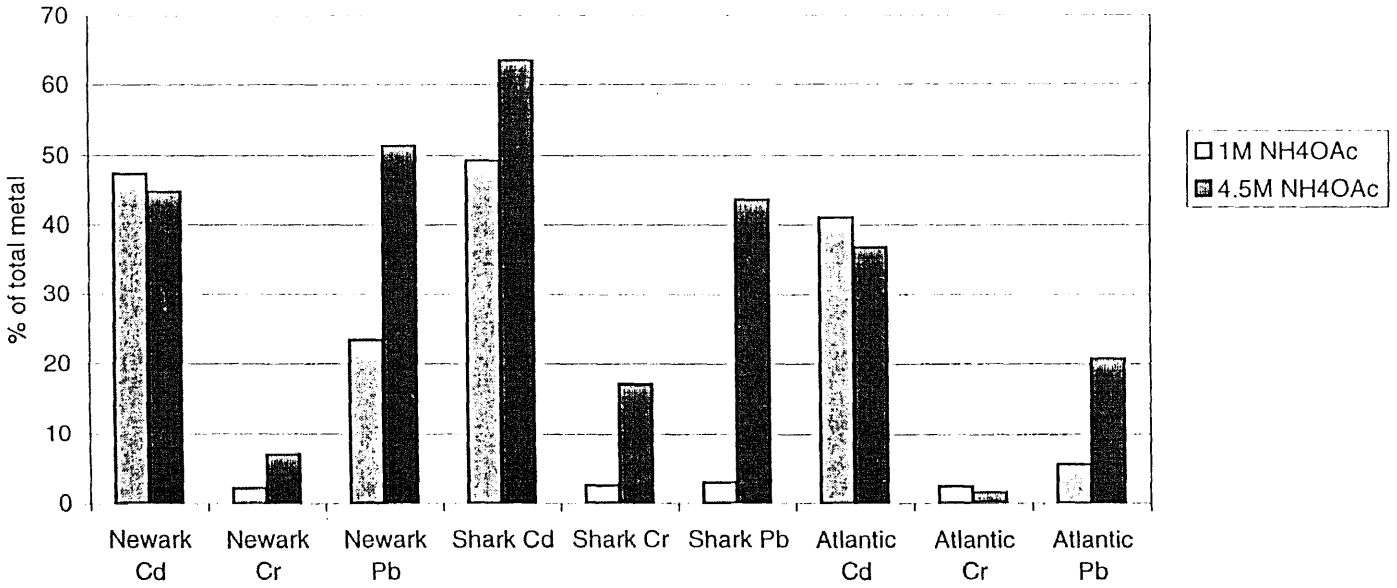


Figure 5.1 Cd,Cr,Pb fractions digested by microwave, 90 sec. from sediments with 1M and 4.5M NH4OAc

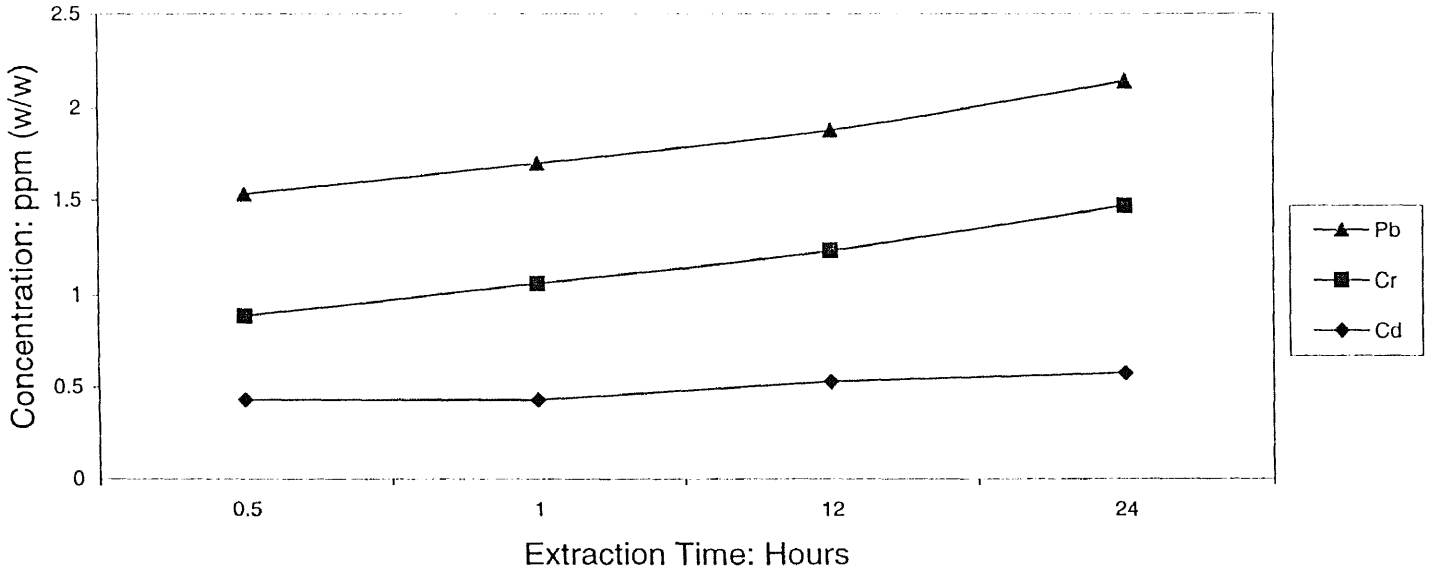


Figure 5.2 Kinetics of exchangeable Cd, Cr, Pb in Atlantic City Bay Sediment by MTM

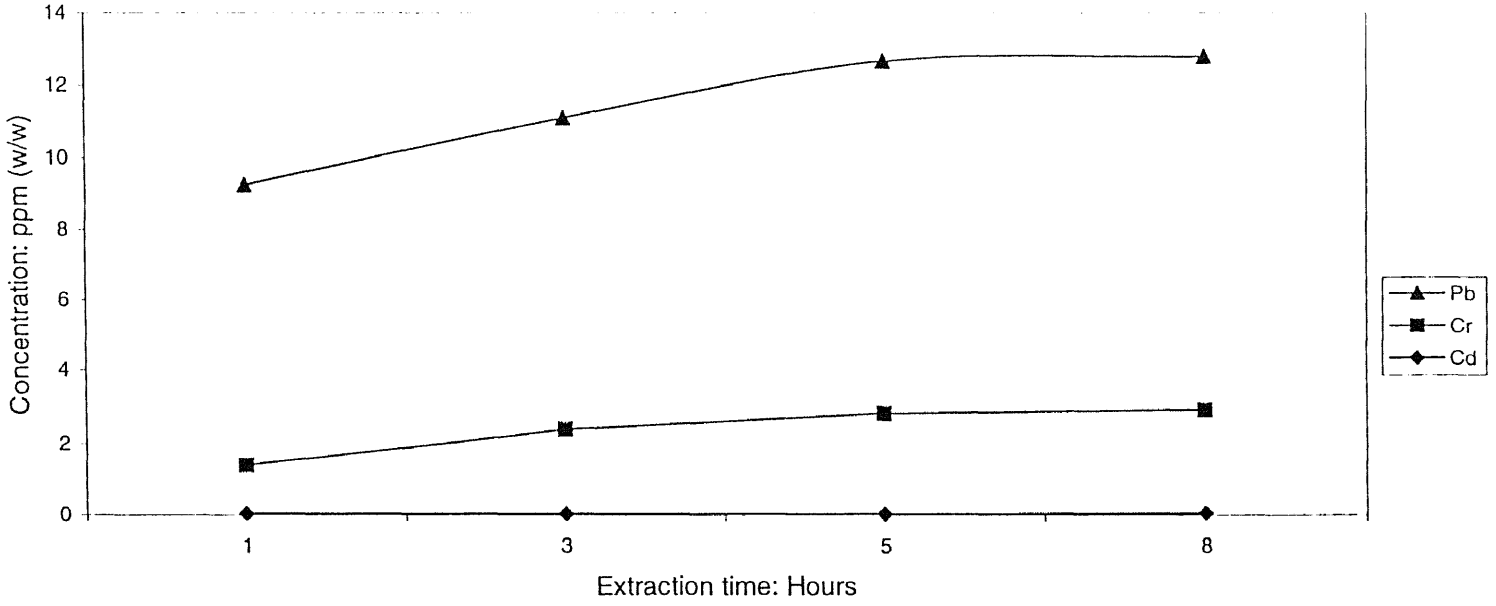


Figure 5.3 Kinetics of Carbonate Cd,Cr,Pb in Atlantic City Bay sediment by MTM

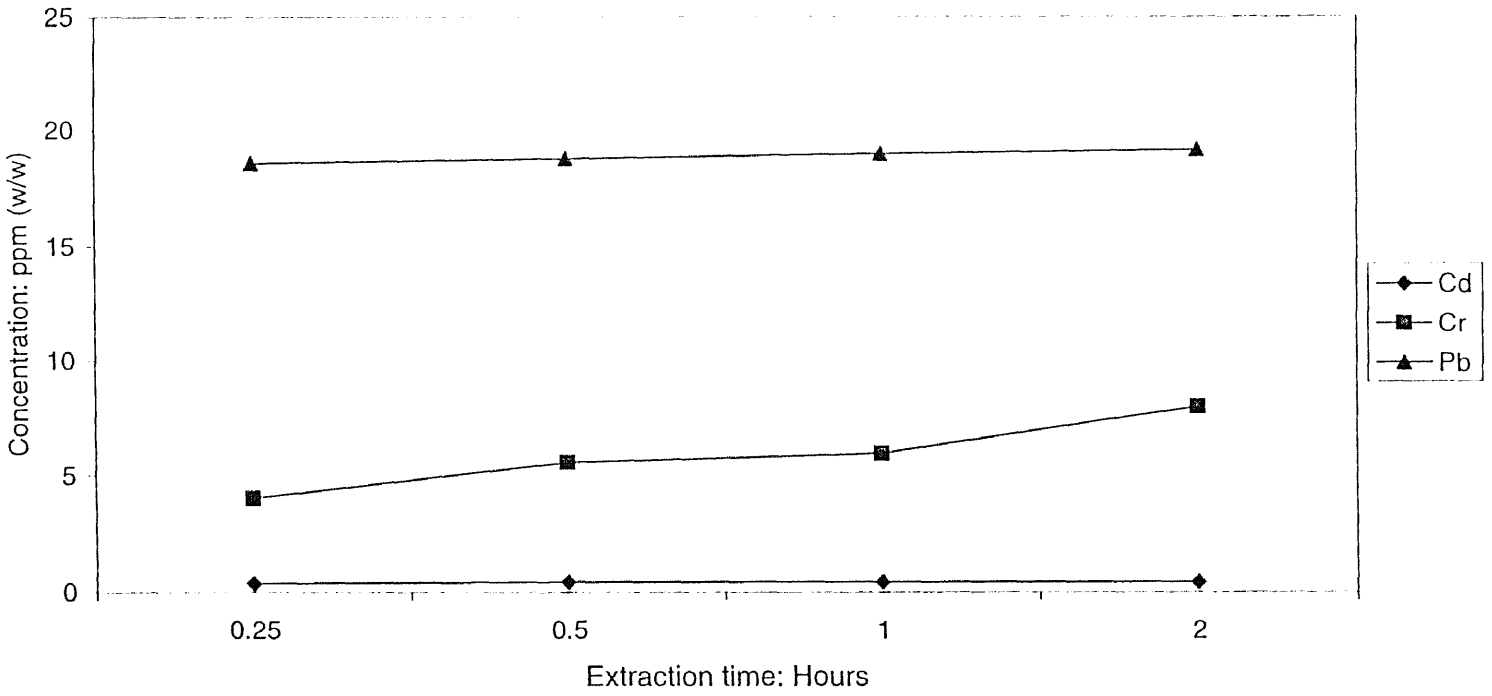


Figure 5.4 Kinetics of Cd,Cr, Pb bound to Fe/Mn-oxide in Atlantic City Bay sediment by MTM

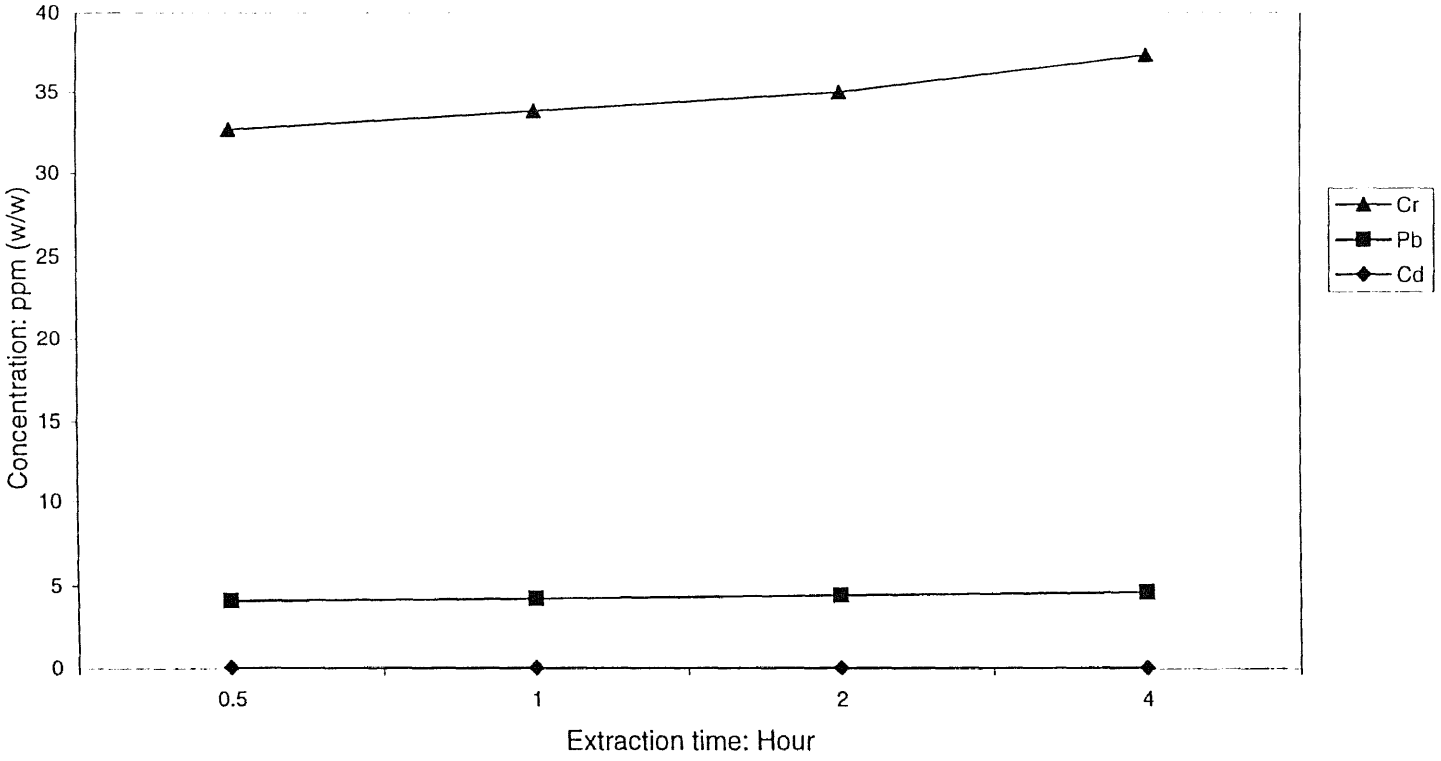


Figure 5.5 Kinetic study on Organic Cd,Cr,Pb in Atlantic City Bay sediment by MTM

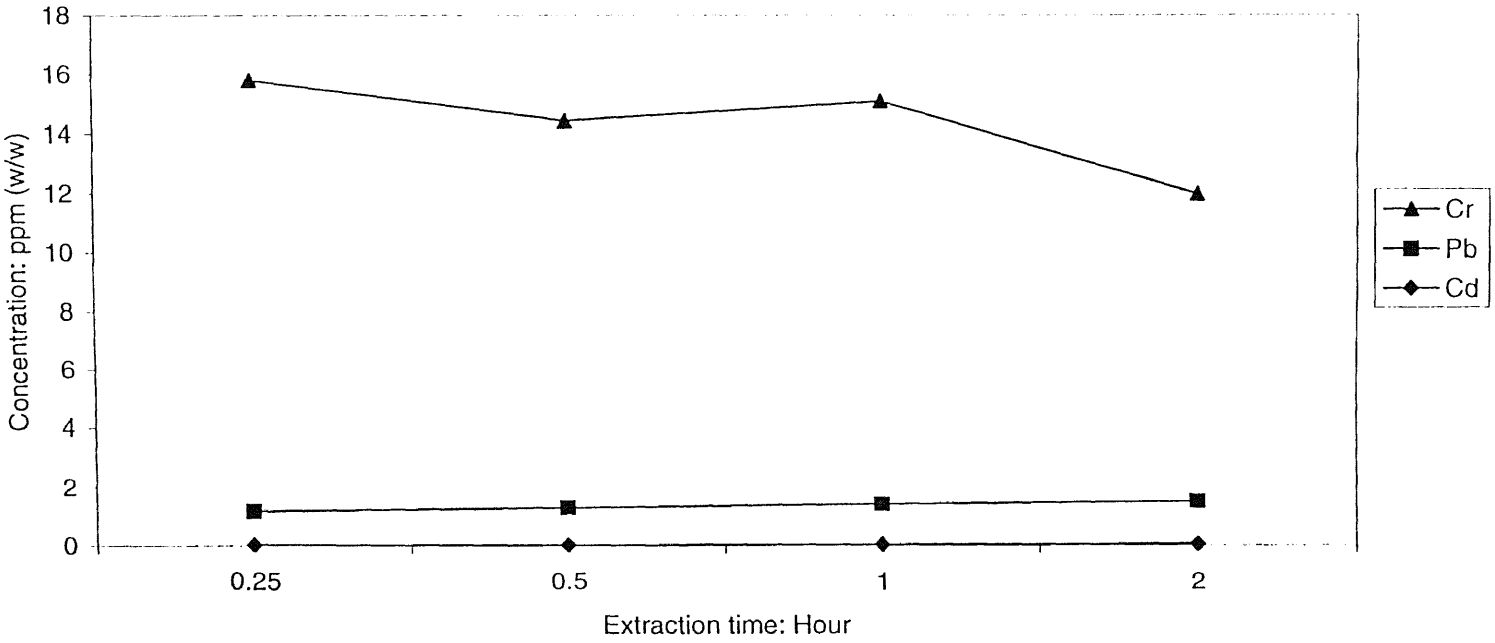


Figure 5.6 Kinetic study on Residual Cd,Cr,Pb in Atlantic City Bay sediment

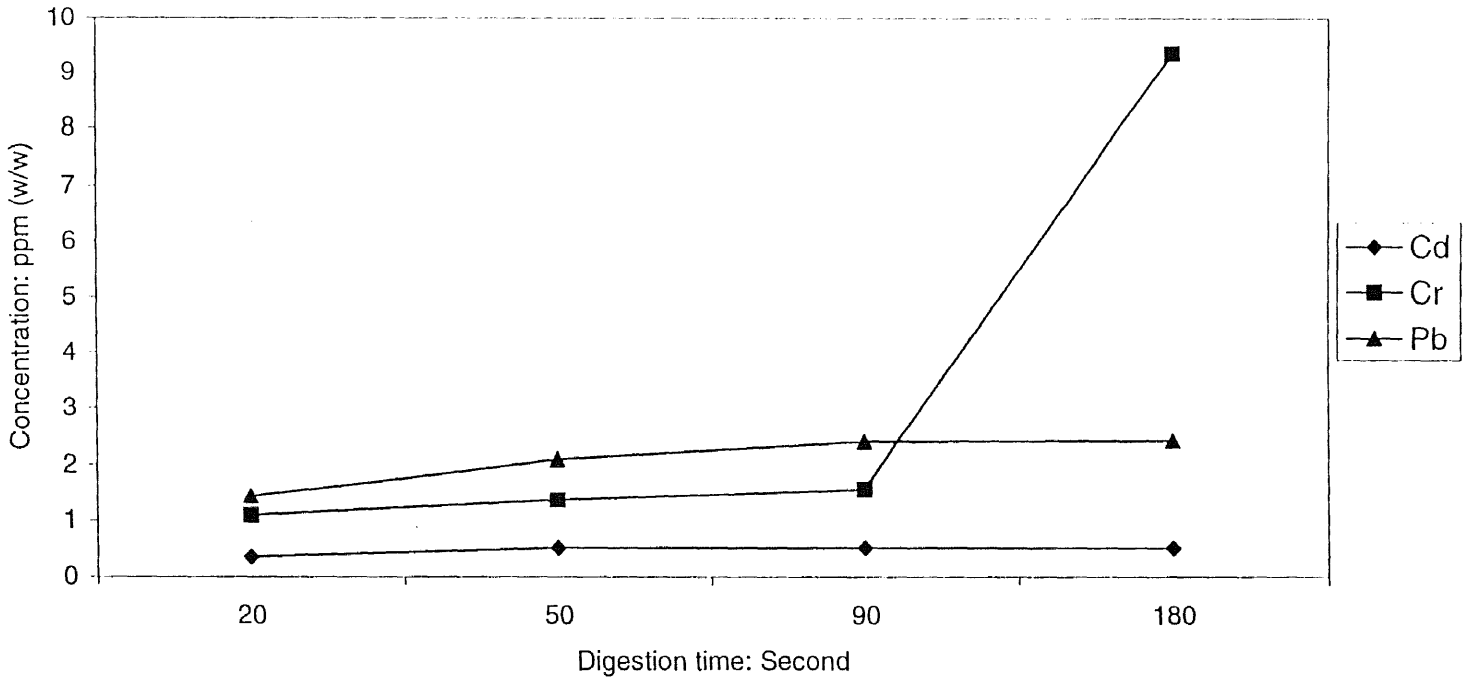


Figure 5.7 Kinetic study on Exchangeable Cd,Cr,Pb in Atlantic City Bay sediment by MWM

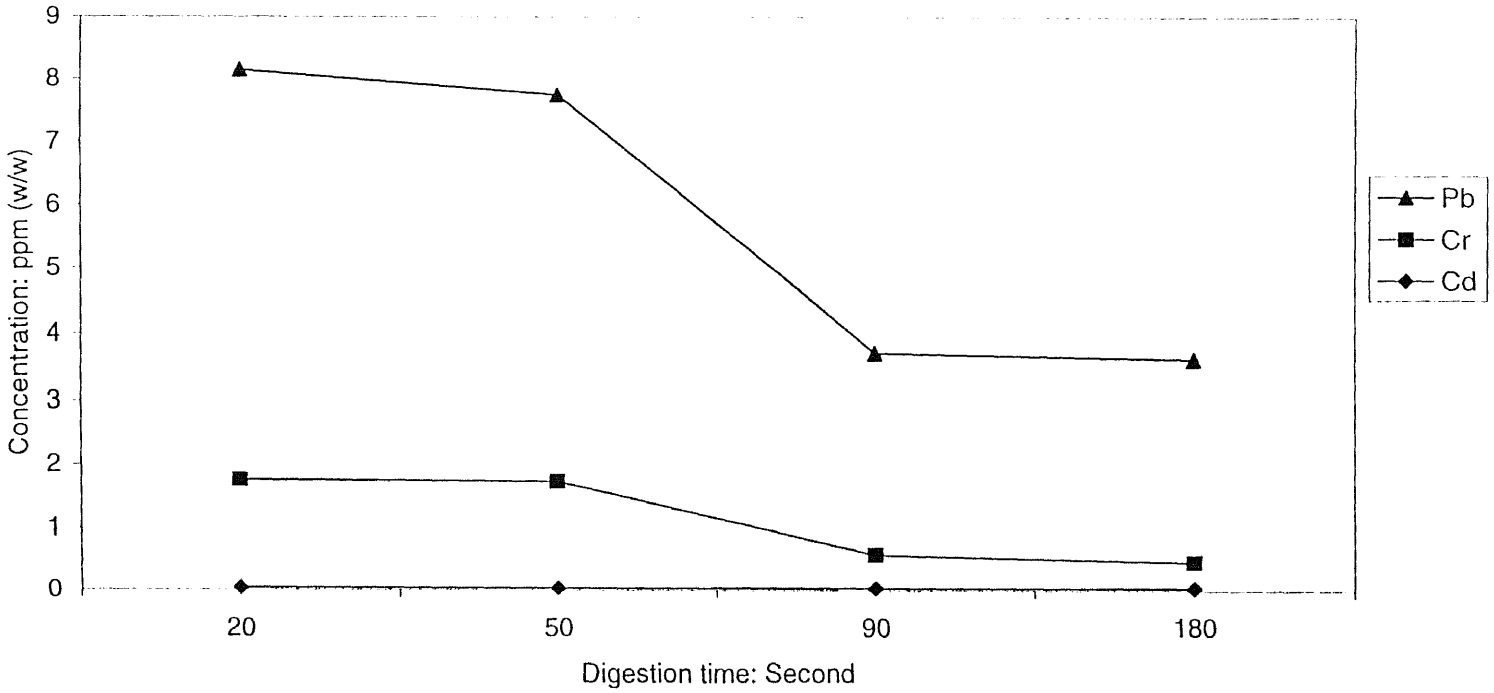


Figure 5.8 Kinetic study on Carbonate Cd,Cr,Pb in Atlantic City Bay sediment by MWM

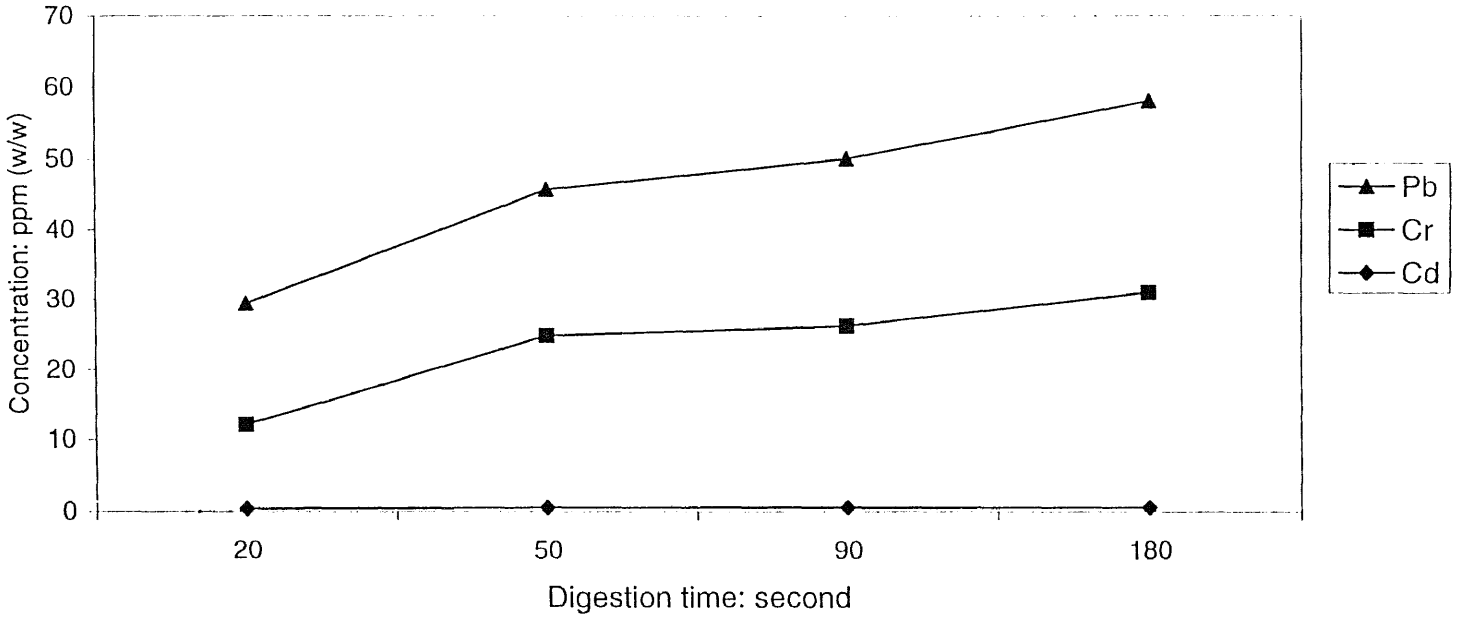


Figure 5.9 Kinetic study on Cd,Cr,Pb bound to Fe/Mn-oxide in Atlantic City Bay sediment by MWM

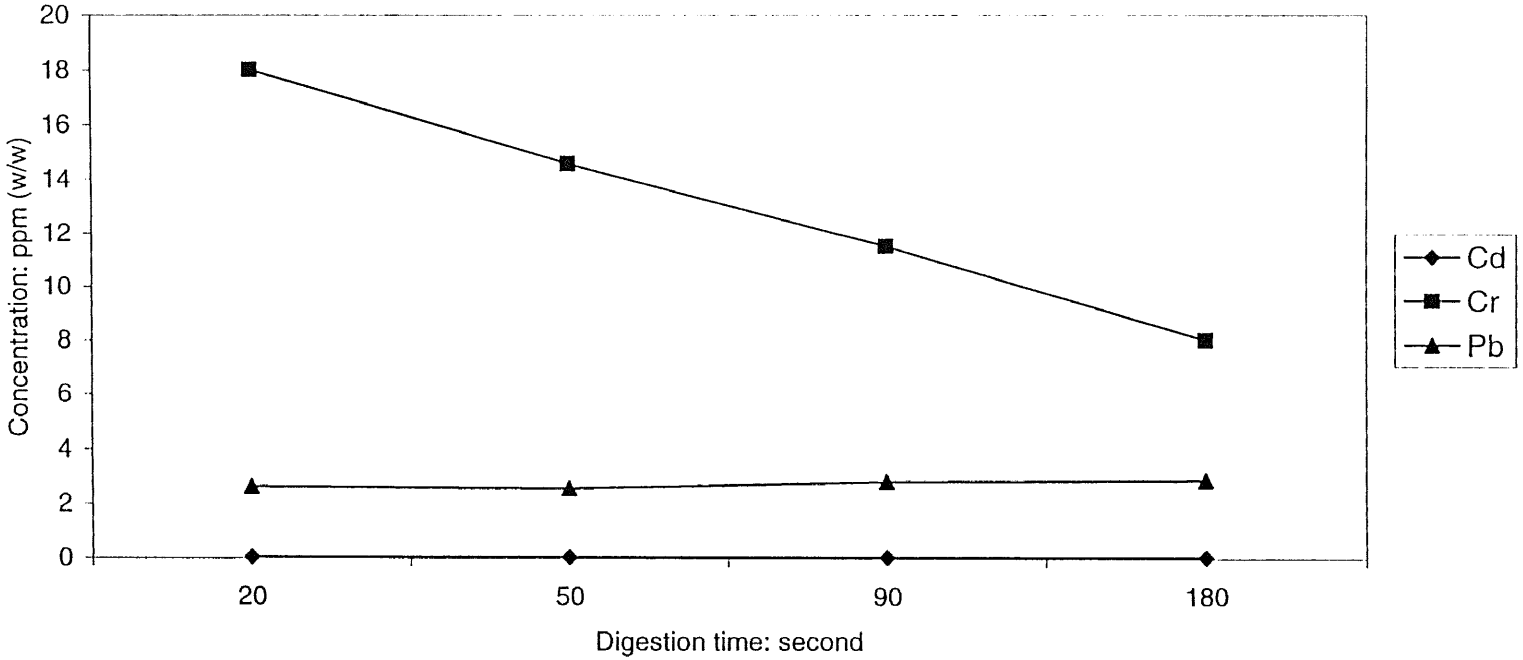


Figure 5.10 Kinetic study on Organic Cd,Cr,Pb in Atlantic City Bay sediment by MWM

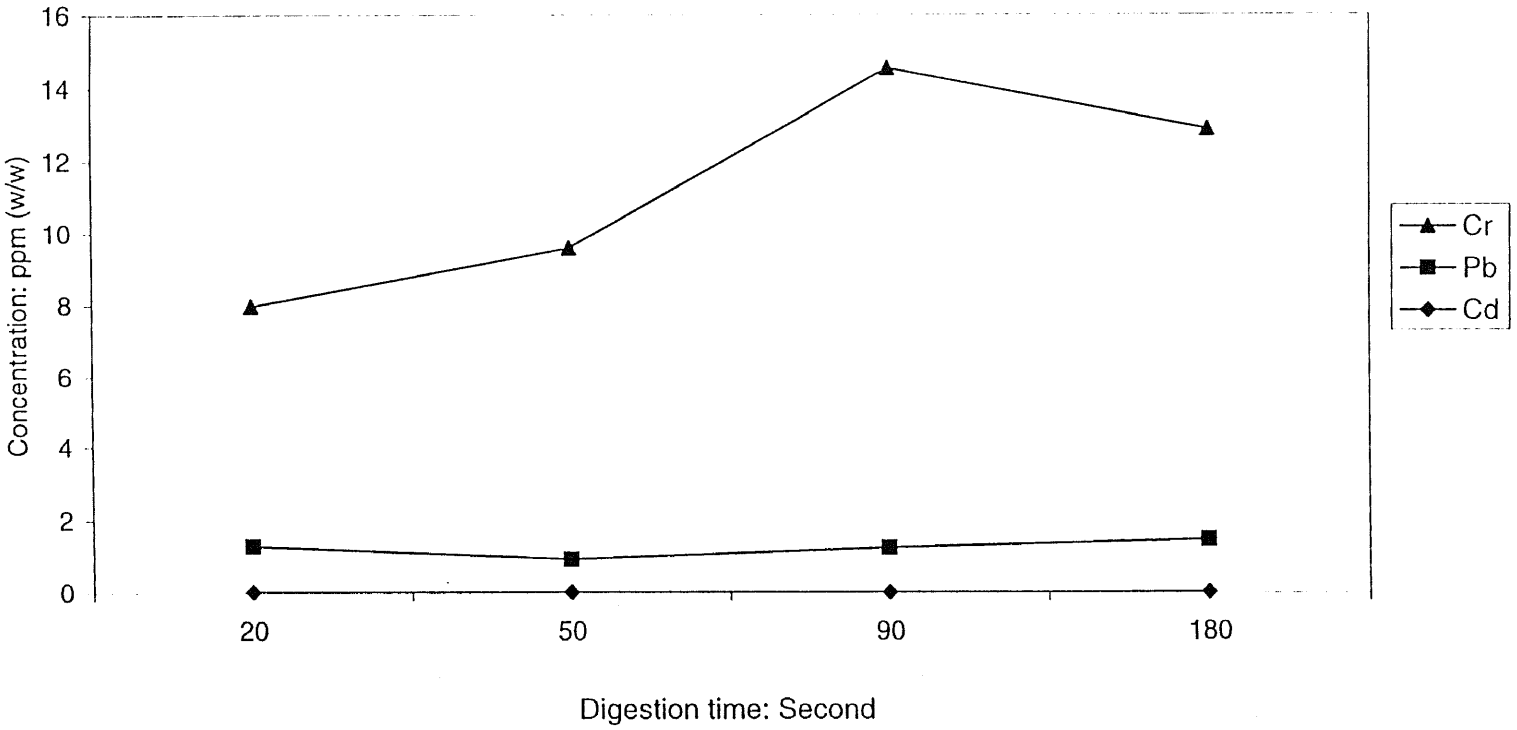


Figure 5.11 Kinetic study on Residual Cd,Cr,Pb in Atlantic City Bay sediment by MWM

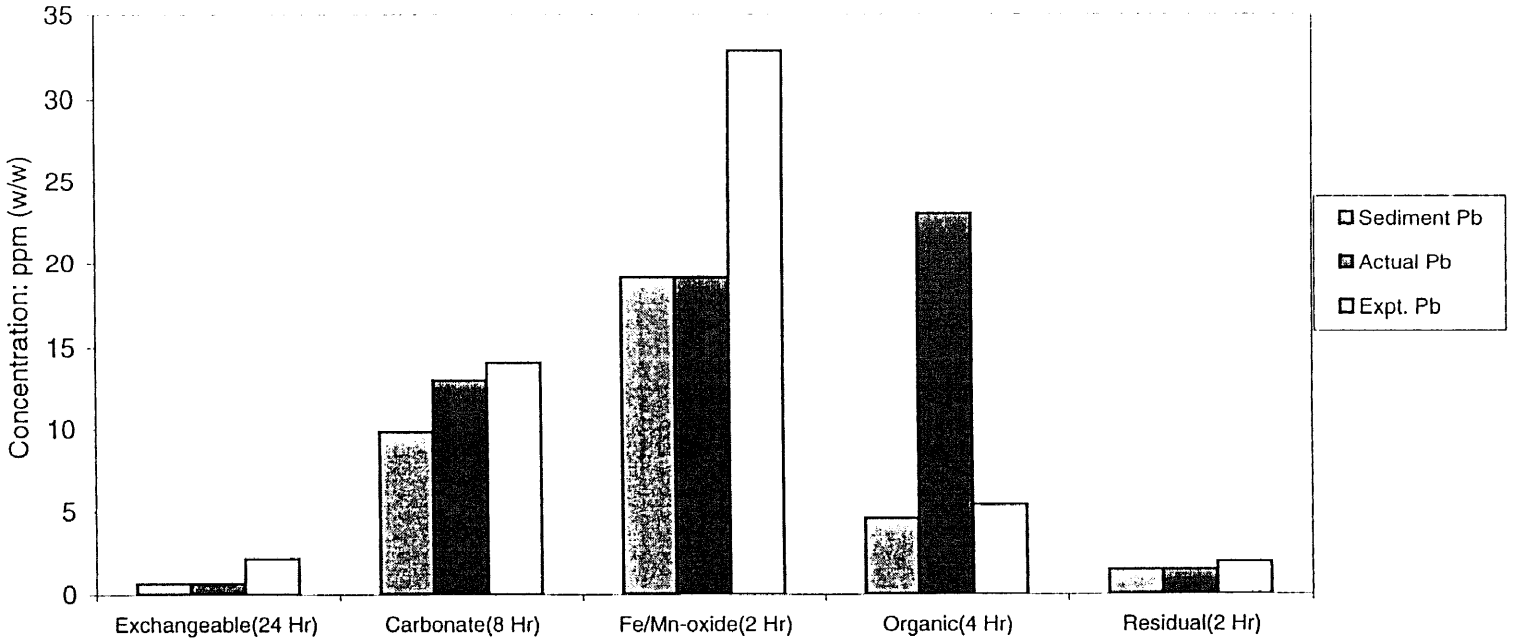


Figure 5.12 Recovery of Pb in Atlantic City Bay sediment by MTM

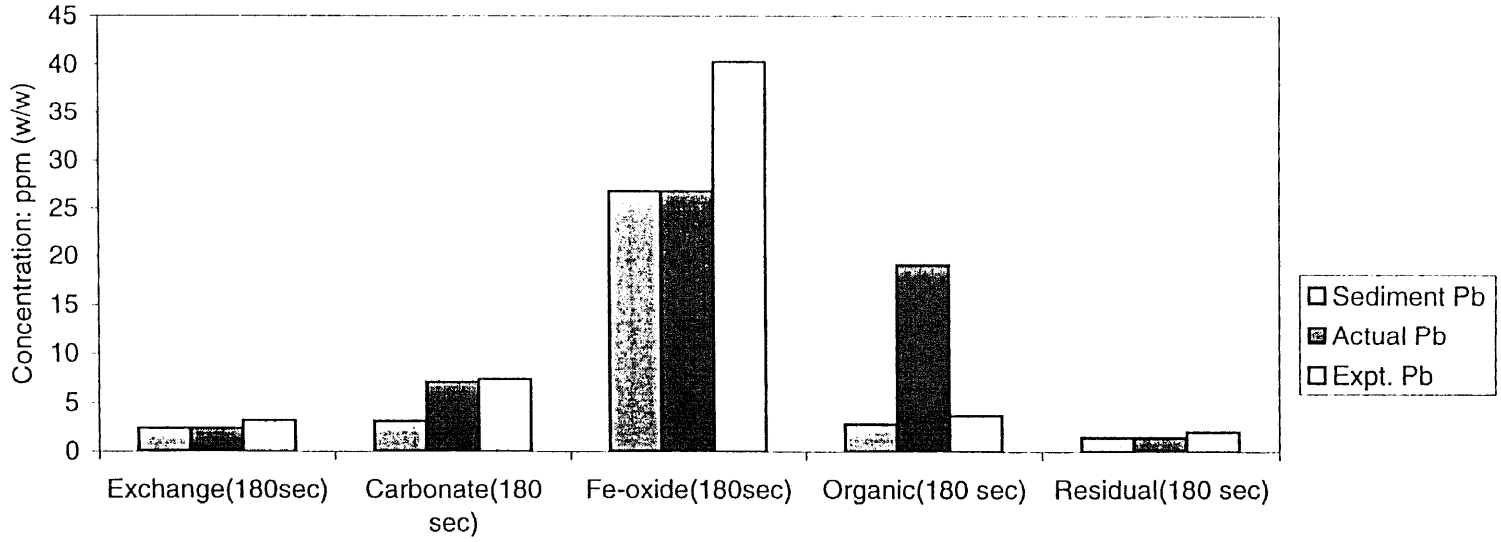


Figure 5.13 Recovery study on Pb in Atlantic City Bay sediment by MWM

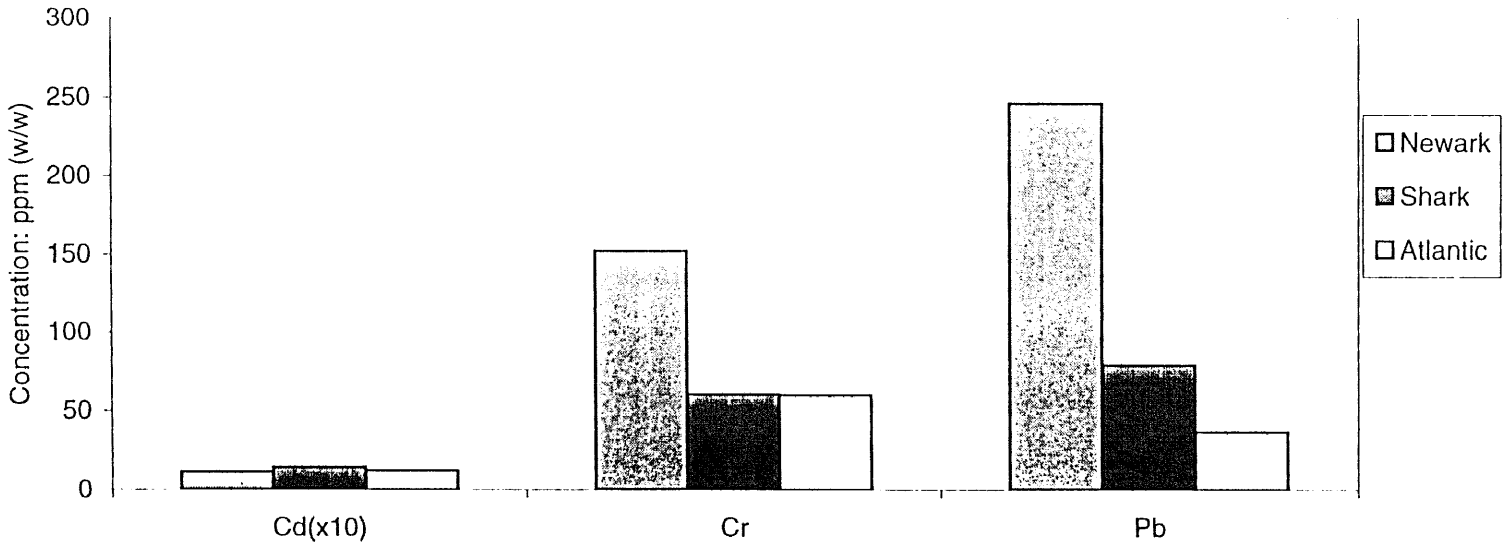


Figure 5.14 Total concentrations of Cd,Cr,Pb in sediments

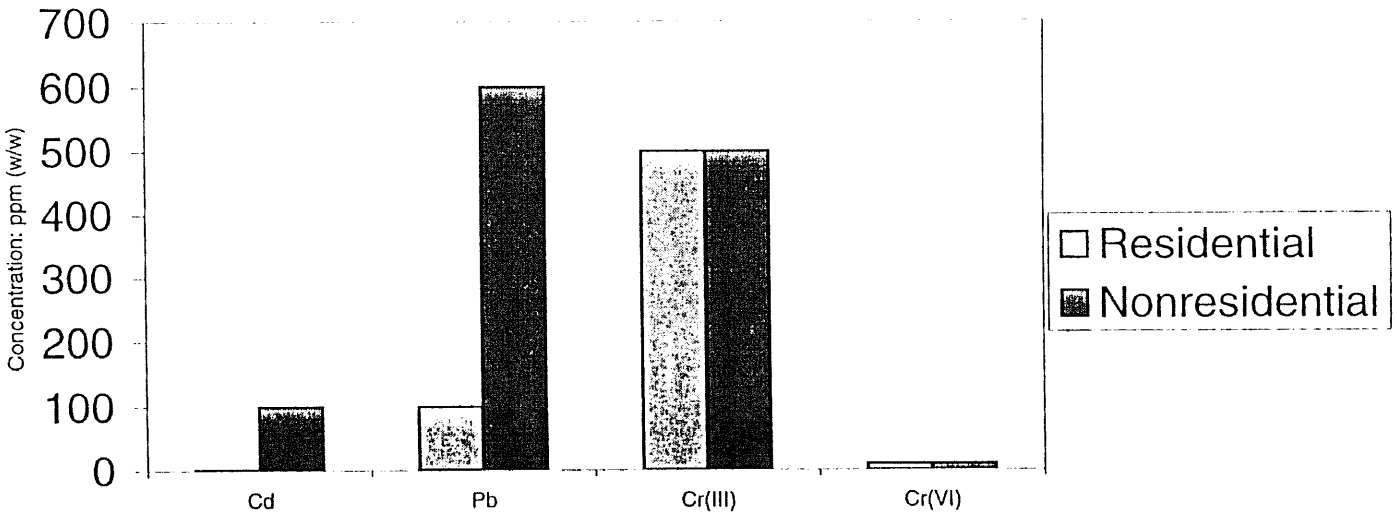


Figure 5.15 NJDEP soil cleanup criteria for Cd,Pb,Cr(III),Cr(VI)

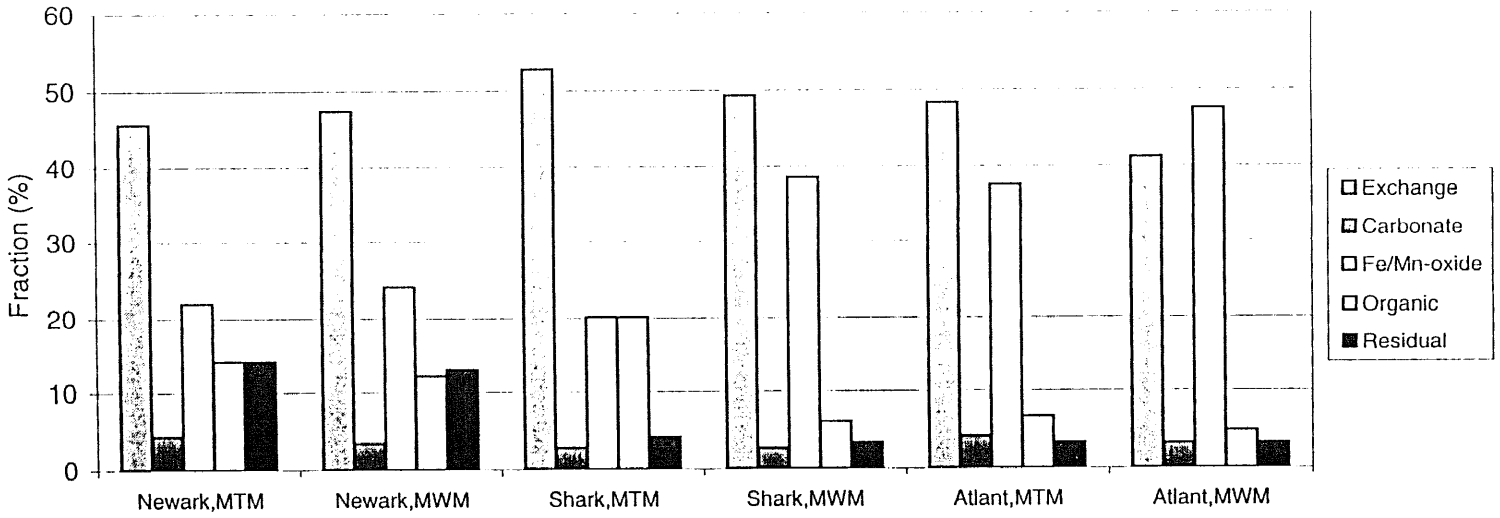


Figure 5.16 Distribution of Cd in different sediment fractions

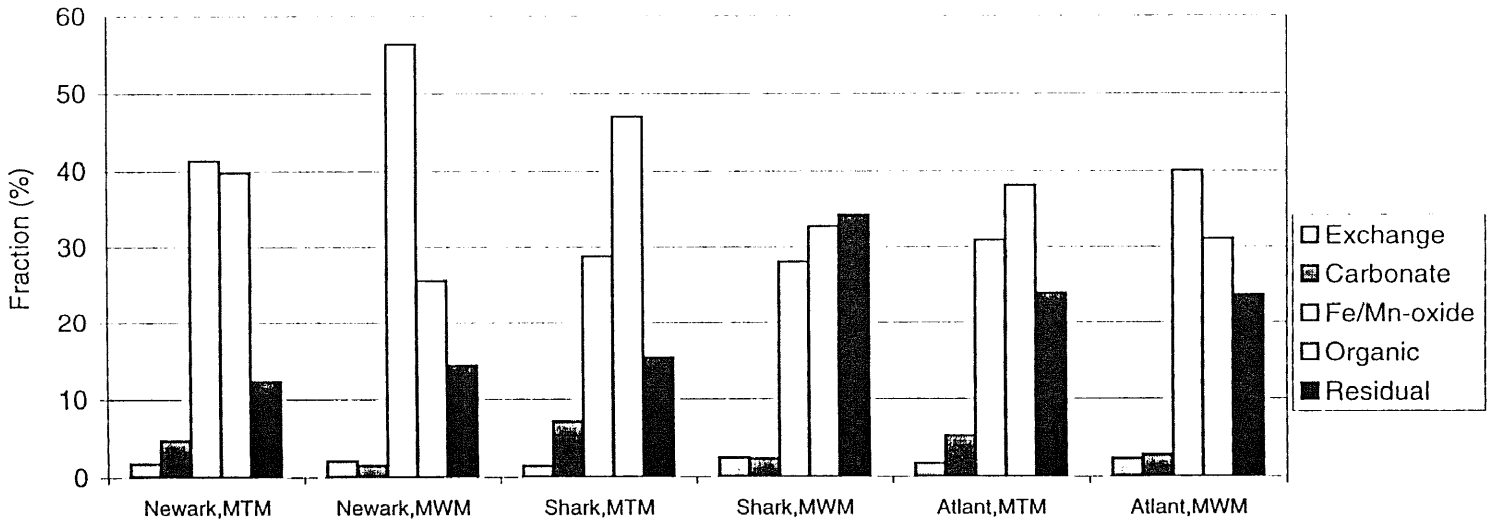


Figure 5.17 Distribution of Cr in different sediments fractions

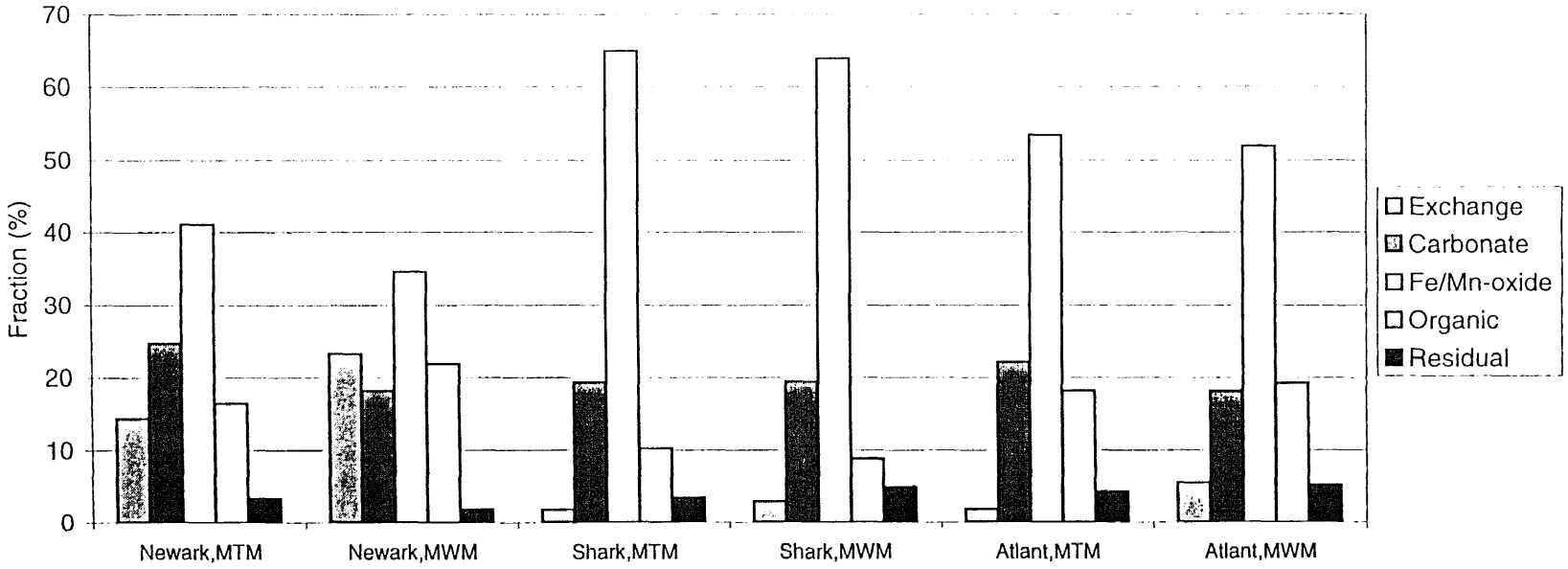


Figure 5.18 Distribution of Pb in different sediments fractions

APPENDIX C - FIGURES FOR CHAPTER 6

DETERMINATION
OF Cd, Cr, AND Pb
IN THE SHARK RIVER ECOSYSTEMS

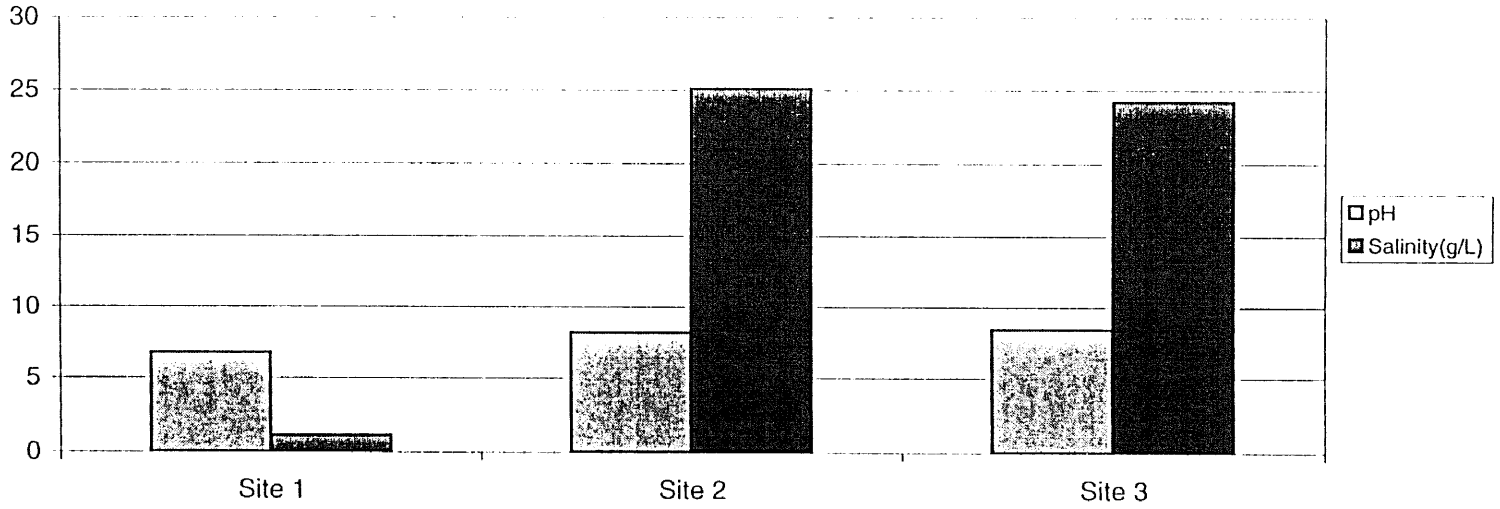


Figure 6.1 pH and Salinity of water samples in Shark River ecosystem

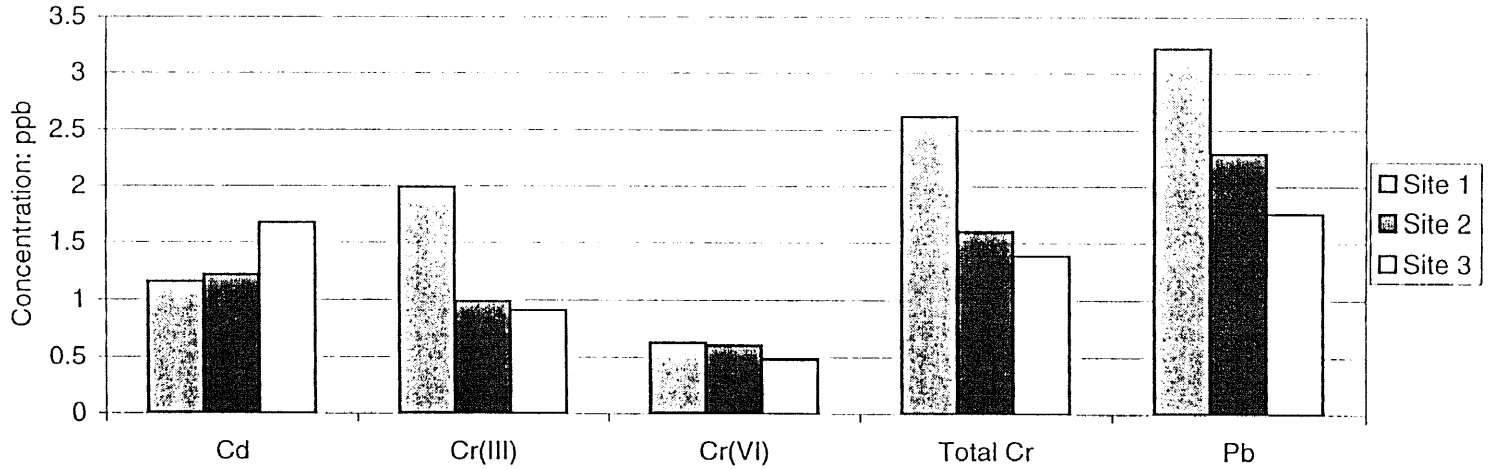


Figure 6.2 Concentration of exchangeable Cd,Cr(III),Cr(VI),Pb in Shark River water

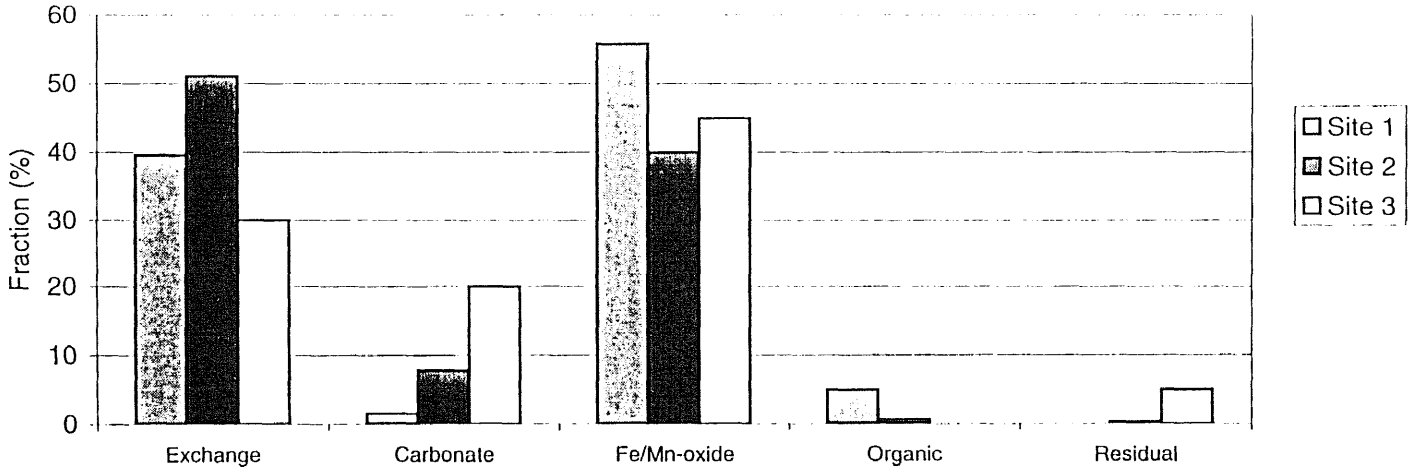


Figure 6.3 Distribution of Cd in Shark River Sediment

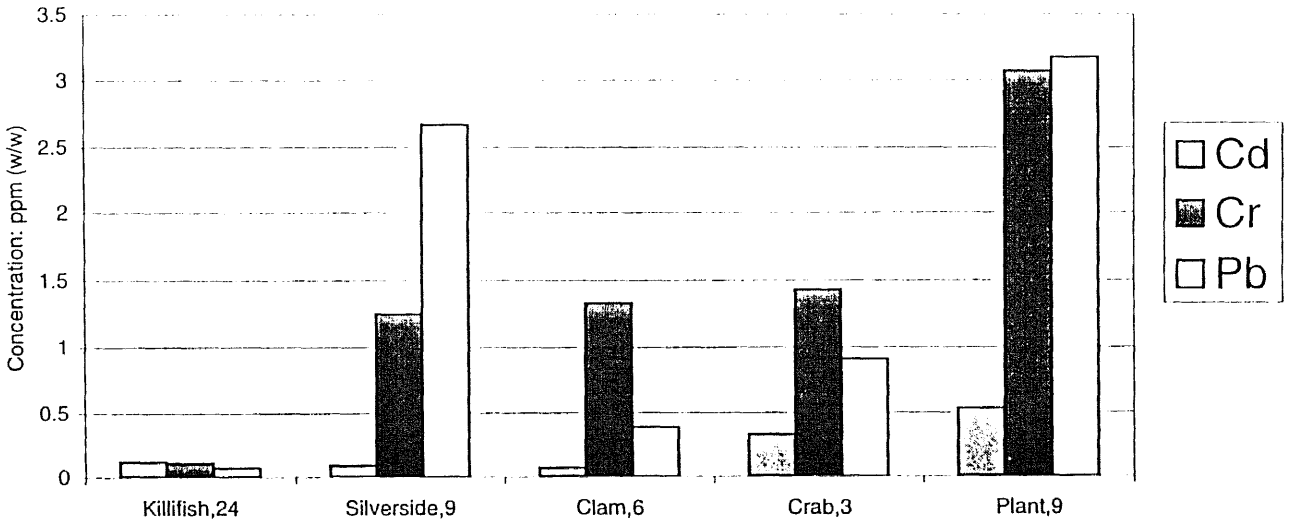


Figure 6.4 Total average concentrations of Cd,Cr,Pb in biota samples from Shark River

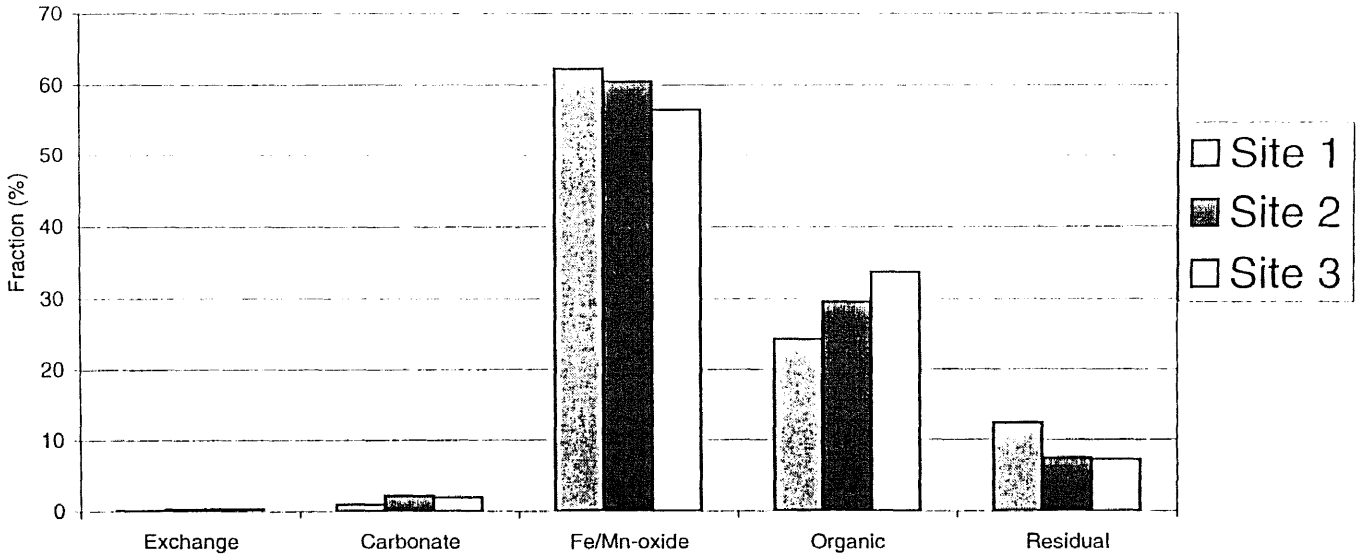


Figure 6.5 Distribution of Cr in Shark River Sediment

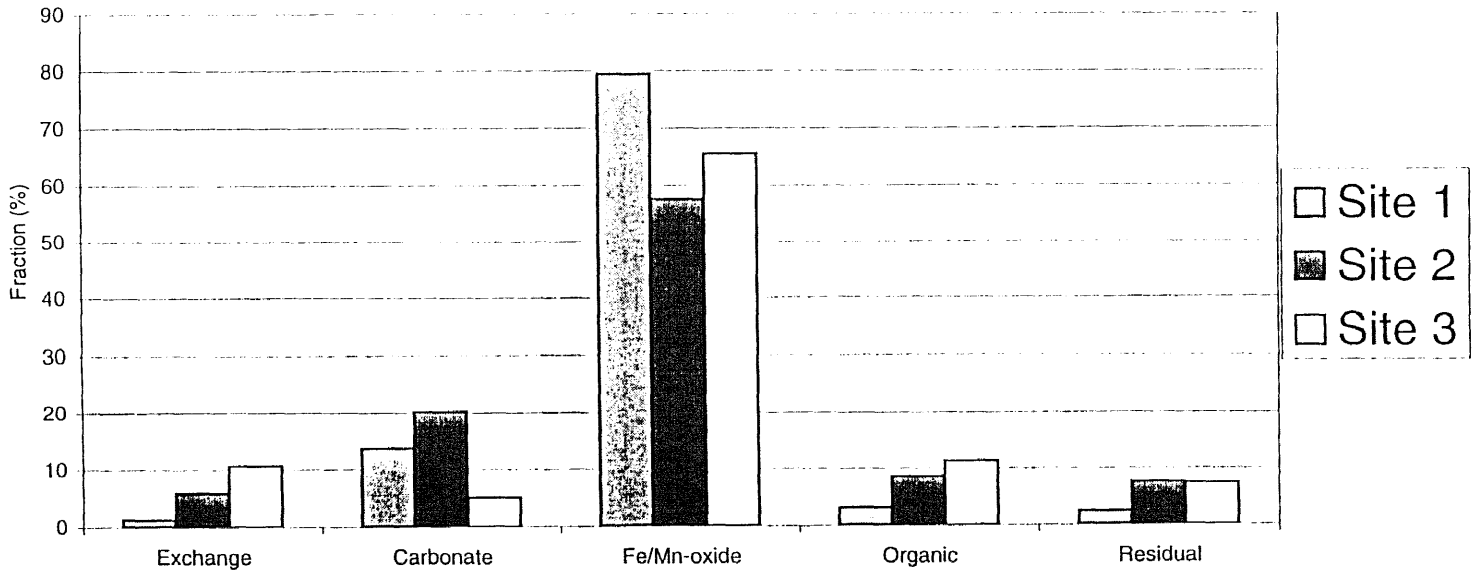


Figure 6.6 Distribution of Pb in Shark River Sediment

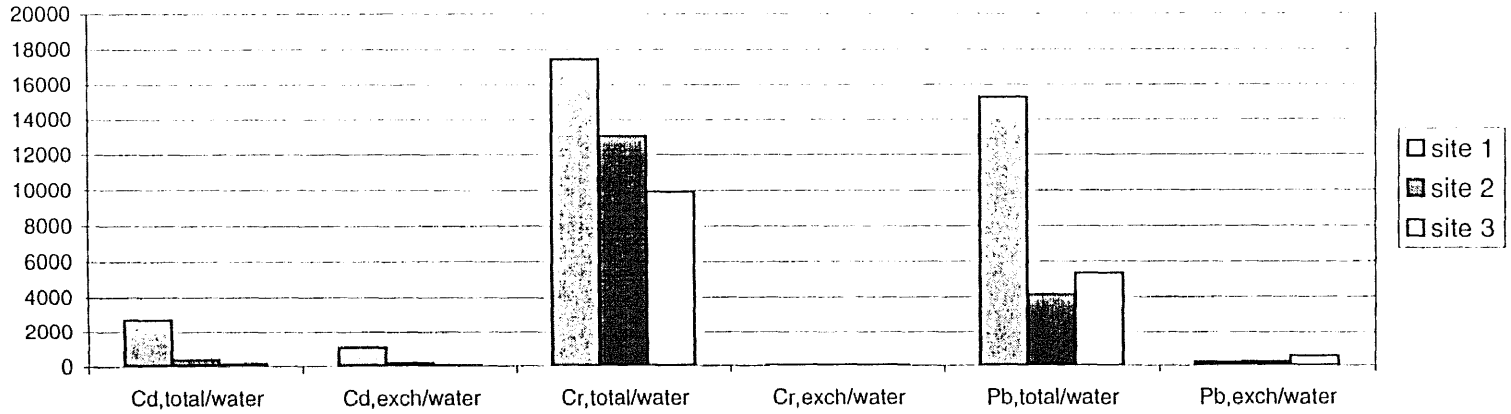


Figure 6.7 Sediment to water ratios for Cd, Cr, Pb for total and exchangeable fraction (Shark River)

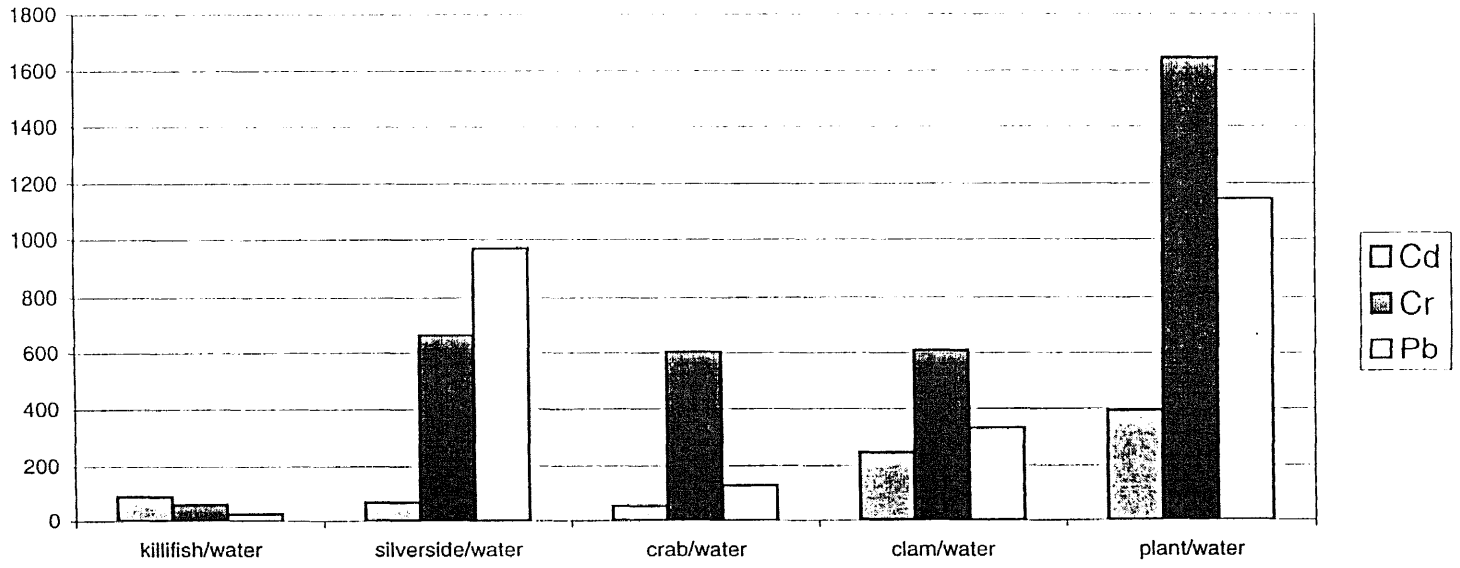


Figure 6.8 Ratios between concentrations in biota and exchangeable concentration in water

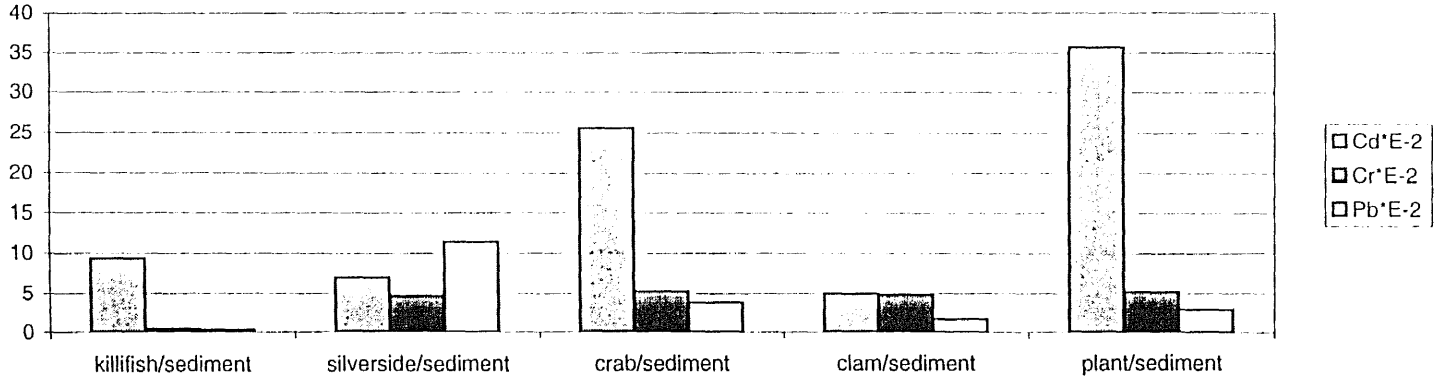


Figure 6.9 Ratios between concentration of trace metals in biota and total concentration in sediment

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